Discipline Specific Elective Paper- III

Nano Materials and Applications

UNIT-I

Nanoscale Systems: Length scales in physics, Nanostructures: 1D, 2D and 3D nanostructures (nanodots, thin films, nanowires, nanorods), Band structure and density of states of materials at nanoscale, size effects in nano systems, Quantum confinement Applications of Schrodinger equation-infinite potential well, potential step, potential box, quantum confinement of carriers in 3D, 2D, 1D nanostructure and its consequences.

UNIT-II

Synthesis of Nanostructure Materials: Top down and bottoms up approach, Photo lithography Ball milling. Gas phase condensation, Vacuum deposition, Physical vapour deposition (PVT): Thermal evaporation, E-beam evaporation, Pulsed Laser deposition,
Chemical vapour deposition (CVD),Sol-Gel Electro deposition, Spray pyrolysis, ,Hydrothemal synthesis, Preparation through colloidal methods, MBE growth of quantum dots.

UNIT-III

Characterization: X-Ray Diffraction, Optical Microscopy, Scanning Electron Microscopy, Transmission Electron Microscopy, Atomic Force Microscopy, Scanning Tunneling Microscopy

UNIT-IV

Applications: Applications of nano particles, quantum dots, nanowires and thin films for photonic devices (LED, solar cells). Single electron devices (no derivation). CNT based transistors. Nonmaterial Devices: Quantum dots hetero structure lasers, optical switching and optical data storage. Magnetic quantum well; magnetic dots, magmetic data storage. Micro Electromechanical Systems (MEMS), Nano Electromechanical Systems (NEMS)

CHAPTER 1

NANOSCALE SYSTEMS

LEARNING OBJECTIVES

- Introduction, Length scales in physics, Nano-structural materials, Band structure of materials at nanoscale.
- Density of states of materials at nanoscale, Size-effects in nano systems

1.0 INTRODUCTION

Nano refers to 10^{-9} and it can be ascribed to any unit of measurement. Hence one nanometre means 10^{-9} metre, one nanosecond means 10^{-9} second, one nanogram means 10^{-9} gram and similarly for other physical units. One nanometre is on the scale of atomic diameter. In a one nanometre line four to five atoms can be placed side by side. Human hair is nearly 10^5 nanometre thick.

Nanoscience is the study nano-structures and nano-materials. It is also the study of phenomena on the nanometre scale. The smallest structure made by human has dimension of a few nanometre. In future the possibility of smallest structure will have the dimension of a few nanometre. This is because any structure will be made from atoms. If structures are made small enough then they show change of properties which are useful in the nanometre range. In nano regime the properties of structures are quite different as compared to their bulk structures. If none of the dimensions of the structure is comparable with the de Broglie wavelength of electrons or excition Bohr radius for it then the structure is treated as bulk. A single strand of DNA (Deoxy Ribose Nucliec Acid) is nearly 3 nanometre wide. The diameter of most of the carbon nanometre is also about 3 nanometre.

Nano-structures are the structures on the scale of nanometres. They can be formed on solid surfaces like metals, semiconductors like silicon, carbon based materials and liquids. They can be created by using specialized methods and techniques. Nano-structures can be studied by specialized equipments. The principles of nano-science are now used by scientists and engineers from various disciplines like physics, chemistry, biology and material science for applications in energy, medicine, computing and data storage. Nano-science is an emerging area of a diverse field with very wide applications.

Nano-technology is the manipulation of matter with at least one dimension in the range 1 to 100 nanometres. It is also defined as the manipulation of matter on an atomic, molecular and supra molecular scale. Nano-technology deals with both natural and artificial structures on the nanometre scale. Nano-technology is capable of manipulating single atoms and molecules. Nano-technology has applications in different fields of science such as semiconductor physics, molecular engineering, molecular biology, organic chemistry, nano-fabrication, surface science etc. It is basically the engineering of tiny machines with the ability to build things from the bottom up using the recent developed techniques and to make highly advanced products. Nano-technology is the promising answers to varioius types of problems in all the fields of science and research. It is believed that one day nano-technology will provide solutions to various types of mankind's problems. In future nano-technology may be able to create many new materials and devices with a wide range of applications in nano-electronics, energy production, cosmetics, biomaterials and nano-medicine etc.

Nano-materials lie in the physical regime between bulk macroscopic materials and the molecular compounds.

Solids can be classified into three categories.

(i) Amorphous solids with no long range order.

(ii) Polycrystalline solids with multiple domains and short range order.

(iii) Crystalline solids with long range order and periodicity.

Nano-technology and nano-science focus mostly on nanometre sized crystalline solids. If the size of material is reduced then statistical mechanical effects and quantum mechaical effects come into play. If the material goes into nano-regime with size between 1 to 100 nanometre at least along one dimension then quantum size effect tends to change the electronic properties of the material. Mechanical, electrical and optical properties of the material are also changed upon reaching the nanoregime. The most notable change is the increase in surface area to volume ratio of the nano-materials over the bulk materials. This increase in S/V ratio causes the change in mechanical, thermal and catalytic properties of the materials. The increase in surface to volume ratio for the nano-materials, is due to the fact that in nano-regime upto 50% of the atoms lie at the surface of the nano-structure. Thus the surface is potentially important in dictating the optical and electrical properties of the material in the nano-regime. The increase in surface area is important in applications where S/V ratio plays a vital role, such as in photovoltaics and in catalysis. The changes in properties of materials while going from bulk to nanosize are :

(i) Opaque materials become transparent.
Example - Copper

(ii) Stable materials become combustible.
Example - Aluminium

(iii) Insoluble materials become soluble
Example - Gold

(iv) Chemically inert materials become catalysts.
Example - Gold.

1.1 LENGTH SCALES IN PHYSICS

Every property of a material has a critical length associated with it. For example the critical length for the resistance of the material, is the scattering length which is the average distance travelled by an electron before it is scattered from positive ion cores in the lattice. If the dimensions of a solid becomes comprable to one or more critical lengths then the fundamental physics and chemistry change. The size dependent properties of solids such as electronic structure and mechanical properties change if particles become smaller than the critical size.

The relevant length scales in physics are actually relative to the natural electron or hole length scales in the parent bulk material. These natural length scales can either be referred to by their de Broglie wavelength or by the exciton Bohr radius. Hence a given nanometre size object of one material may be in nano-regime but a similar sized object of another material may not be in the nanoregime. Thus the critical lengths are different in different materials. Bulk materials exhibit continuous absorption and electronic spectra, but when they reach length scales less than or equal to exciton Bohr radius or de Broglie wavelength both optical and electronic spectra become discrete and more atomic like.

A nano-material is in the quantum confinement regime if its size is less than the corresponding de Broglie wavelength of an electron or hole. It is also said that "A nano-material is quantum confined because its size is less than the correponding exciton Bohr radius.

Both these statements have the same meaning and they are equivalent to each other.

Bohr radius of an electron is given by

$$r_0 = \frac{4\pi \epsilon_0 \hbar^2}{m e^2} \qquad \ldots(1)$$

where, $\epsilon_0 = 8.85 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2}$

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34}\ Js$$

$m = 9.1 \times 10^{-31}$ kg,

$e = 1.6 \times 10^{-19} C$

Using equation (1) we get

$r_0 = 0.528 \times 10^{-10}$ m

or $r_0 = 0.528$ Å

This is the standard value of Bohr radius of an electron.

If the electron is not in vacuum then the Bohr radius is given by

$$r_0 = \frac{4\pi \epsilon \hbar^2}{m e^2} \qquad \ldots(2)$$

Now the permittivity of the medium is give by

$$\epsilon = \epsilon_0 \epsilon_r$$

where ϵ_r is the dielectric constant of the medium.

Using equation (2) we get,

$$r_0 = \frac{4\pi \epsilon_0 \epsilon_r \hbar^2}{m e^2} \quad \ldots(3)$$

An excition is the bound electron-hole pair in a semiconductor. Hence exciton Bohr radius is the distance between electron and hole in this pair.

The exciton Bohr radius is given by

$$r_e = \frac{4\pi \epsilon_0 \epsilon_r \hbar^2}{m_{eff} e^2} \quad \ldots(4)$$

where m_{eff} is effective mass of exciton and is given by

$$m_{eff} = \frac{m_e m_h}{m_e + m_h} \quad \ldots(5)$$

where, m_e = effective mass of electron.

m_h = effective mass of hole

If λ is the de Broglie wavelength of an electron then we can write

$$2\pi r_e = n\lambda \quad \ldots(6)$$

Hence de Broglie wavelength on the exciton Bohr radius are the natural length scales by which we can compare the physical size of nano-materials. Objects with dimensions less than de Broglie wavelength or exciton Bohr radius, will exhibit quantum confinement and will manifest drastically changed properties as compared to their bulk materials.

1.2 NANO-STRUCTURAL MATERIALS

Nano-structured materials based on the dimensions of their structural elements are mainly of four types :

(i) Zero dimensional (0D) nano-structured materials
(ii) One dimensional (1D) nano-structured materials
(iii) Two dimensional (2D) nano-structured materials
(iv) Three dimensional (3D) nano-structured materials

0D Nano-structured materials

Zero dimensional (0D) nano-structured materials are the materials in which nanoparticles are isolated from each other. These materials include nano-cluster materials and nanodispersions. Nanodots or quantum dots and magnetic quantum dots are zero dimensional (0D) nano-structured materials. The Degree of Freedom of 0D Nano-structured materials is zero :

The motion of 0D nano-materials is confined in all the three directions and the particle is not free to move at all. The particle has quantized energies associatated with its motion along the three directions.

1D Nano-structured materials

One dimensional (1D) nano-structured materials are materials with length from 100 nonometre to tens of microns. These materials include nanofibres and nanotubular materials. Nanorods, nanotubes and nanowires are 1D nano-structured materials. The degree of freedom of 1D nano-structured materials is one. The motion of 1D nano-structured materials is confined along two directions and they are free to move along only one direction. The particle has quantized energies associated with the directions of confinement.

2D Nano-structured materials

Two dimensional (2D) nano-structured materials are materials with nanometre thickness. These materials are referred as single layer materials. These are crystalline materials consisting of a two dimensional single layer of atoms. These materials include nanosheets, nanoribbons, nanomehses, graphene coats, and films. The degree of freedom of 2D nano-materials is two. The motion of 2D nano-structured materials is confined along one direction and they are free to move along the rest two directions. The particle has discrete (quantized) energies associated with the directions of confinement.

3D Nano-structured materials

Three dimensional (3D) Nano-structured materials are bulk materials. These materials are compact or consolidated (bulk) polycrystals with nanosize grains. These materials include powder, fibrous, multilayer and polycrystalline materials. The degree of freedom of 3D nano-structured materials is three and they are not confined at all. They are free to move along all the three directions. There is no quantization of the motion of the particle and the particle has a continuous range of energies between a minimum and maximum.

1.2.1 Nanodots

Nanodots are zero dimensional nano-structures in which there is confinement along all the three directions. Nanodots are also known as quantum dots. Magnetic nanodots are being developed for future information storage. Nanodot could potentially store over one hundred times more data than the present hard drives. Nanodots can be considered as tiny magnets which can switch polarity to present a binary digit. Hard drive magnetizes areas 200-250 nm long to store individual bits but nanodot can be 50 nm in diameter or smaller. Hence Nanodot can offer consdierably higher information density than the recent hard drives. Nanodots could also lead to ultrafast memory.

1.2.2 Thin Films

Thin films are two dimensional nano-structures in which there is confinement along one direction. A thin film is a layer of material ranging from fractions of a nanometre to several nanometres in thickness. Thin films are created through a process called deposition. Deposition is a thin film

coating process which is achieved by modifying the four states of matter such as solid, liquid, gas and plasma. Some applications of thin film technology are electronic semiconductor devices which include integrated circuit chips, micro-fabricated mechanisms, micro electromechanical systems (MEMS), micro electronic optical systems and light emitting diodes. Other applications of thin films technology are optical coatings, photovoltaic solar cells and thin film batteries. The performance of a thin film optical coating is enhanced when the thin film coating consists of multiple layers having varying thicknesses and refractive indices. Ferromagnetic and ferro-electric thin films are used as computer memory. Thin film technology is used to reduce the cost of photovoltatic systems which are used to collect solar energy. Thin films battries can be deposited into chips of any shape or size. Thin films can be printed onto plastic, thin metal or paper using thin film printing technology. Thin film technology is used in the manufacturing of reflective or antireflective or self-cleaning glass.

1.2.3. Nano wires

Nanowires are one dimensional nano-structures in which there is confinement along two directions. A nanowire is a nano-structure with the diameter of the order of a nanometer. The ratio of the length to width is greater than 1000 for a nanowire. Nanowire can be defined as the structures having a thickness contrained to tens of nanometers or less and an unconstrained length. At such scale quantum mechanical effects are important. Hence nanowires are also known as quantum wires.

The following types of nanowires exist.

(i) Superconducting nanowire
Example - YBCO

(ii) Metallic nanowires
Example - Ni, Pt, Au

(iii) Semiconducting nanowires
Example - SiNW, InP, GaN

(iv) Insulating nanowires
Example - SiO_2, TiO_2

(v) Molecular nanowires
Example - Organic nanowire (DNA)
Inorganic nanowire ($Mo_6 S_{9-x} I_a$)

1.2.4 Nano Rods

Nanorods are one dimensional nano-structures in which there is confinement along two directions. A Nanorod is a nano-structure with dimensions range from 1 to 100 nm. Nanorods can synthesized from metal, or semiconducting materials. For Nanorods the ratio of length to width is between 3 and 5. Nanorods are produced by direct chemical synthesis. One potential application of Nanorod is in display technology. This application is due to the fact that the reflectivity of the rods can be changed by changing their orientations with an applied electric field. Another

use of nanorods is in microelectro-mechanical systems (MEMS). Nanorods along with other metal nano-particles also act as theragnostic agents. Nanorods are used as cancer therapeutics because they absorb heat in the IR region and generate heat when excited with IR light. Nanorods are used in the treatment of tumors. Nanorods based on semiconducting materials have also been investigated for application as energy harvesting and light emitting devices. ZnO nanorods have the potential for application as novel sources of near ultraviolet radiations.

1.3 BAND STRUCTURE OF MATERIALS AT NANOSCALE.

In crystalline solids the electronic energy levels are different from that of a single atom because the potential characterization of the crystalline structure is a periodic function in space whose value at any point is the result of contribution of each atom. The inner-shell electrons of the individual atoms in crystalline solids are not affected by the neighbouring atoms but the energy levels of the outer shell electrons are changed since these electrons are shared by all the neighbouring atoms. Hence the new energy levels will be determined by the quantum mechanical treatment, which results in the formation of energy band of closly spaced energy levels of outer-shell electrons instead of widely separated energy levels in an isolated atom as shown in the Fig-1.3(a).

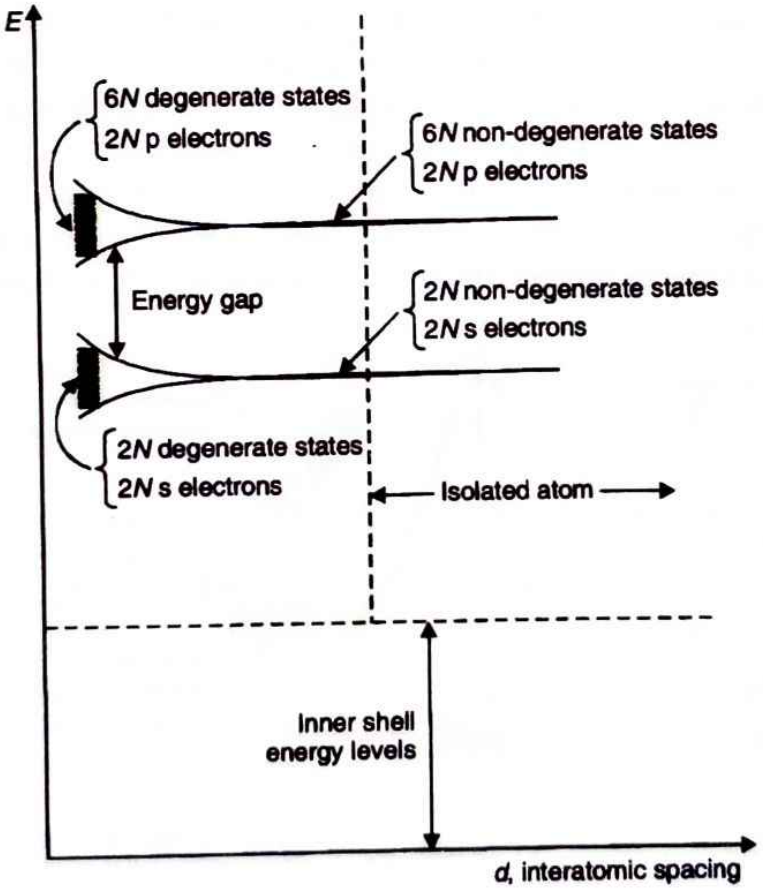


Fig. 1.3(a) Schematic diagram of the splitting of energy levels of isolated atoms to energy bands due to coupling between atoms.

The band structure of a solid crystal (energy-momentum, E-K, relationship) is obtained by solving the Schrodinger equation of an approximate single election problem.

Consider some group-IVA materials (C – $1s^2 2s^2 2p^2$, Si – $1s^2 2s^2 2p^6 3s^2 3p^2$
Ge – $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Sn – $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$)

having partially filled p – orbitals. The p – orbital has six possible states out of which two are filled but s – orbital has all the two possible states filled by electrons Neglecting the influence of inner shell energy levels, if we consider N isolated atoms of any one the above elements then the 2N s-electrons will fill all the 2N possible s-levels with identical energy and 2N p – electrons will fill one third of the possible 6N p-states, all at the same energy as shown in the Fig-1.3.(a). If the atoms are brought close to each other, the atoms will interact with each other and the atomic wave function will overlap. The electronic energy levels will become degenerate and spread out in energy according to the Pauli's exclusion principle, due to the coupling between atoms. Hence 2N s – states and 6N p – states will spread into the respective 2N and 6N discrete states. The separation between the discrete states will be very small because N is very large and of the order of 10^{23} cm^{-3}. These closely spaced energy levels are treated as quasi-continuous states and called energy bands as shown in the shaded region of Fig.1.3.(a). The 2N s – states will be completely filled with 2N s – electrons but 6N–P states will be partially filled with 2N–P electrons. The energy gap E_g between the two bands decreases with the decrease in the inter atomic spacing and now the interaction between the atoms becomes very large. The energy band structure depends on the crystal structure of the materials and the electronic configuration of the atoms of the material. The Schrodinger equation for the band structure will become complicated and the solutions will lead to an approximate band structure as shown in the Fig.1.3.(b). For very small interatomic distances the s – band and p – band overlap to give a total 8N (6N – p levels + 2N s-levels) allowed energy levels, out of which half will be occupied by 4N (2N s-electron + 2N p - electrons) electrons. These electrons could not be identified as s – electrons or p – electrons of individual atoms and they would belong to the crystal as a whole. Hence the above elements are tetravalent in nature. At the lattice spacings the band structure will consist of completely filled valence band with 4N valence electrons an upper band called conduction band, separated by energy gap called for bidden gap (E_g)as shown in the Fig.1.3(b).

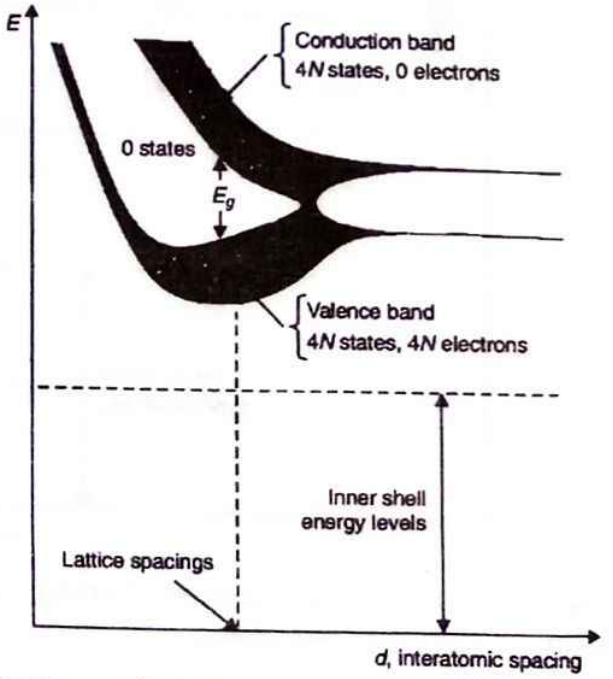


Fig. 1.3(b) Schematic diagram of the formation of valence band and conduction band at lattice spacings

The electronic band structures are usually associated with crystalline materials. The quasi crystalline and amorphous solids may also exhibit band structures. The periodic nature and symmetrical properties of crystalline materails make it much easier to examine the band structures of these materials. The well defined symmetry axes of the crystalline materials make it possible to determine the dispersion relationship between momentum and energy of a material.

1.3.1 Energy – band structure

Electrical conduction is produced within a material due to the motion of charge carriers under the influence of an applied electric field. A material is a conductor if it contains a large umber of free charge carriers. In metals the valence electrons from the atoms form a cloud of electrons due to the nature of metallic bonding. These electrons in the electron cloud are free to move within the metal and called conduction electrons. A material with a very poor conductivity is called an insulator or non-conductor. A material having conductivity, between conductors and insulators, is called semiconductors, In general, insulators and semiconductors do not have metallic bonding. The range of conductivities shown by different solids is described in Fig.1.3.1(a) According to electrical conductivity materails can be classified into conductors, semiconductors and insulators. The metals are excellent conductors, insulators are poor conducto of electrons and semiconductors lie between conductors and insulators.

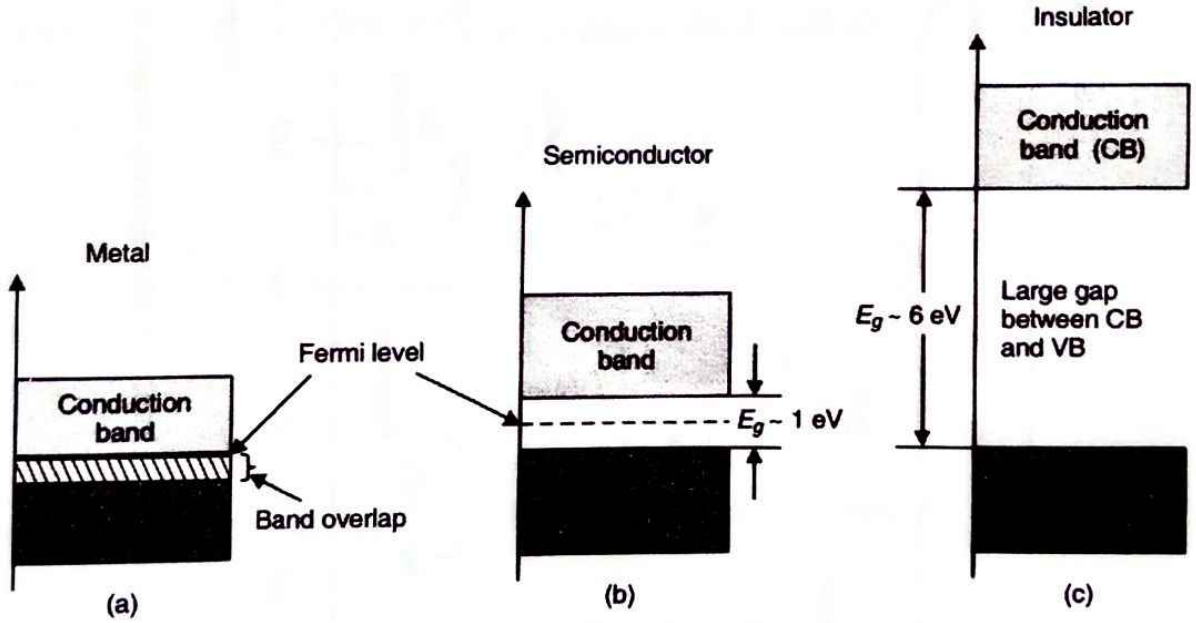


Fig. 1.3.1 Schematic energy band structures of (a) metals, (b) semiconductors and (c) insulators.

According to band structure materials can also classified into three categories, e.g conductors, semiconductor and insulators. Metals have partially filled conduction band and under the influence of an external electric field the electrons gain additional energy and move to higher states and constitute electric current. In metals the conduction band and the valence band overlap with each other as shown is the Fig.1.3.1(b).

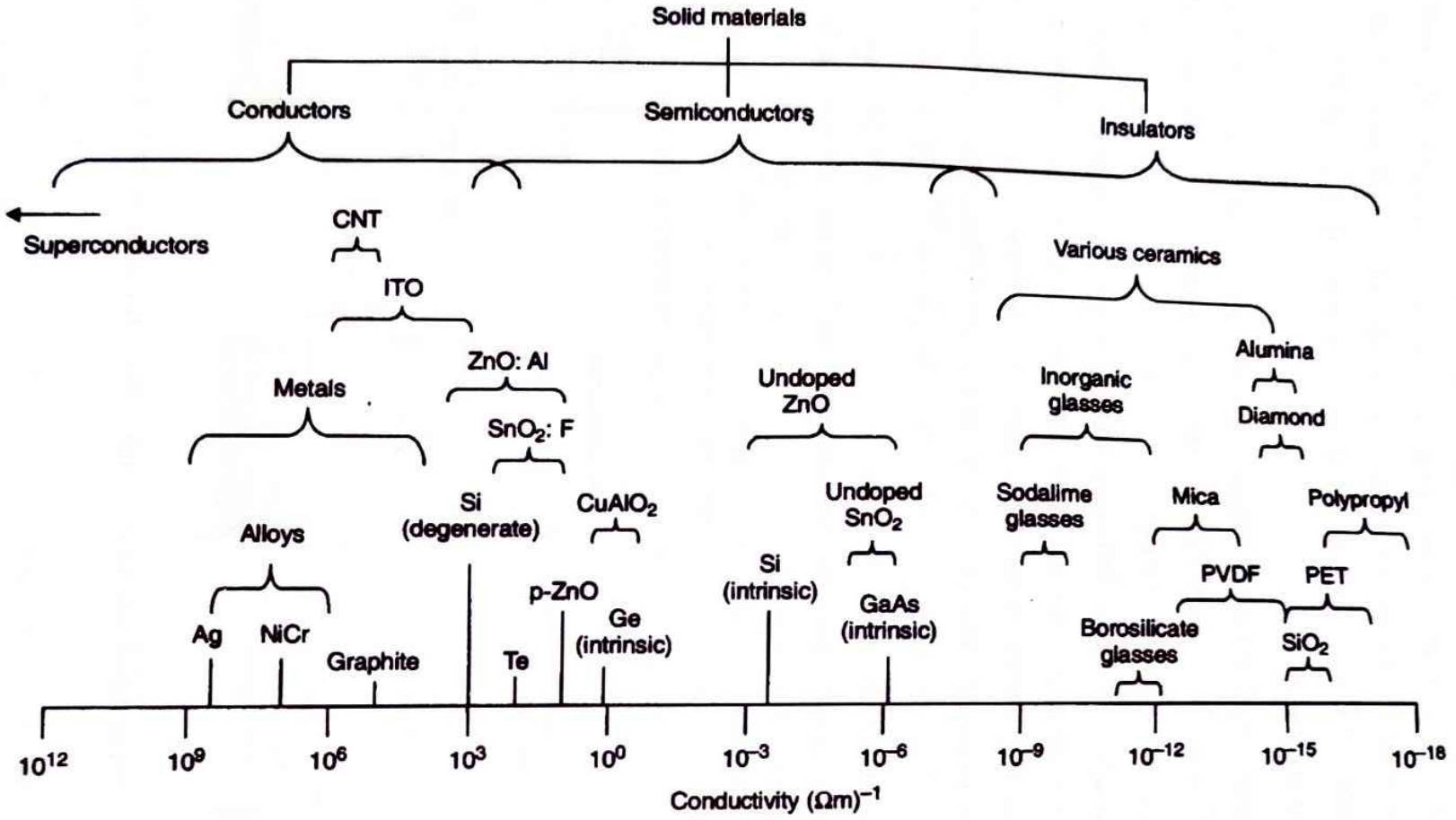


Fig. 1.3(b) Conductivity ranges of various materials (after Ref. [1]).

In insulators the energy gap (E_g) is very large ($E_g \simeq 6eV$). Hence at room temperature the electrons cannot gain sufficient energy to jump from filled valence band to empty conduction band. Therefore the insulators are poor conductors of electrons. The band-structure of the insulators is shown in Fig.1.3.1(d). In semiconductors, the energy gap (E_g) is very small ($E_g \simeq$ leV). Hence at room temperature the electrons can gain sufficient thermal energy to jump from filled valence band to vacant conduction band. These conduction electrons participate in the conductivity under the influence of an external applied electric field. The empty states in the valence band are known as holes which also act as the carrier of electricity. If temperature is increased them more electrons jump from valence band to conduction band. Hence the conductivity of semiconductors increases with the increase in temperature. The band structure of semiconductors is shown in Fig.1.3.1(c).

The forbdden energy gap or band gap (E_g) is an important parameter for semiconductors. It was found that energy gap (E_g) decreases with the increase in temperature. The functional relation for E_g is given by

$E_{gT} = E_{g0} - 3.6 \times 10^{-4}T$

Where E_{g0} = energy gap at 0K

E_{gT} = energy gap at TK

T = increase in temperature,

SOLVED EXAMPLES

Example – 1

Find the band gap of S_i at 300K if the band gap at 0K is 1.21.eV.

Ans. For S_i

$E_{g0} = 1.21eV$

$T = 300K$

Now $E_{gT} = E_{g0} - 3.6 \times 10^{-4}T$

or $E_{gT} = 1.21 - 3.6 \times 10^{-4} \times 300$

or $E_{gT} = 1.21 - 3.6 \times 3 \times 10^{-2}$

or $E_{gT} = 1.21 - 0.108$

or $E_{gT} = 1.102eV$

Example – 2

Find the band gap of Ge at 300K if the band gap at OK is 0.785eV.

Ans. For Ge

$E_{g0} = 0.785eV$

$T = 300K$

Now $E_{gT} = E_{g0} - 3.6 \times 10^{-4}T$

or $E_{gT} = 0.785 - 3.6 \times 10^{-4} \times 300$

or $E_{gT} = 0.785 - 0.108$

or $E_{gT} = 0.677eV$

Example 3

Find the forbidden band gap of S_i at 400K if the forbidden band gap at OK is 1.21eV.

Ans. For S_i

$E_{g0} = 1.21eV$

$\therefore E_{gT} = E_{g0} - 3.6 \times 10^{-4}T$

or $E_{gT} = 1.21 - 3.6\,5\,10^{-4} \times 400$

or $E_{gT} = 1.21 - 0.144$

or $E_{gT} = 1.066eV$

Example – 4

Find the forbidden energy gap of Ge at 400K if the forbidden energy gap at OK is 0.785eV

Ans. For Ge

$E_{g0} = 0.785eV$

$\therefore E_{gT} = E_{g0} - 3.6 \times 10^{-4}T$

or $E_{gT} = 0.785 - 3.6 \times 10^{-4} \times 400$

or $E_{gT} = 0.785 - 0.144$

or $E_{gT} = 0.641eV$

1.4 DENSITY OF STATES OF MATERIALS AT NANOSCALE

The energy and volume density of electronic energy levels in a crystalline solid, change across the energy band. The number of electronic energy levels corresponding to the electronic wave functions in the solid crystal in the central region of the band are expected to be very large as shown in the Fig 1.4(a). Hence the number of electronic energy levels per unit volume over the energy interval E ~ E + dE are known as the density of states (DOS) and defined as ρ (E) dE where ρ (E) is the density of states.

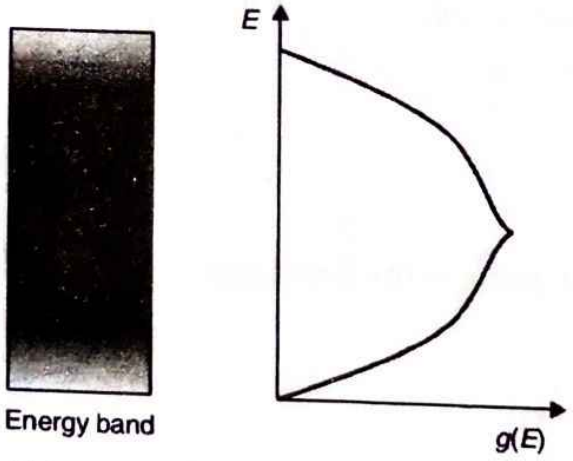


Fig.1.4(a) Density of states across an energy band.

Hence the number of electronic energy states per unit volume up to some energy E′ will be

$$N_v(E') = \int_0^{E'} \rho(E)\,dE \qquad \text{---- (1)}$$

The density of states for a 3D crystal is expressed as

$$\rho(E)_{3D} = \frac{1}{2\pi^2}\left(\frac{2m'}{\hbar^2}\right)^{\frac{3}{2}}(E-E_p)^{\frac{1}{2}} \quad \text{..... (2)}$$

Where m' is the electron effective mass in a band, E_p is the potential energy which may be the conduction band edge (E_c) or valence band edge (E_v) and $\hbar$ is the reduced form of Planck's constant i.e. $\hbar = \frac{h}{2\pi} = 1.0546 \times 10^{-34}$ Js.

For a 2D structure like quantum well the confinement of carriers in one spatial direction results in the fermation of quantum states formotion in this direction. Hence the density of states for 2D structure is modified and can be expressed as

$$\rho(E)_{2D} = \frac{m'}{\pi\hbar^2}\sum_i H(E-E_i) \quad \text{..... (3)}$$

Where $H(E-E_i)$ is the Heaviside function which takes the value of zero when E is less than E_i and one when E is equal to or greater than E_i and E_i is the ith energy level within the 2D structure.

For a ID structure like quantum wire the motion of charge carriers is allowed only in one direction and the other two directions are quantized. Hence the density of states for ID structure is expressed as

$$\rho_{(E)_{ID}} = \frac{1}{\pi}\left(\frac{2m'}{\hbar^2}\right)^{\frac{1}{2}}\sum_i \frac{n_i H(E-E_i)}{(E-E_i)^{\frac{1}{2}}} \quad \text{..... (4)}$$

Where n_i is the degeneracy factor.

For a 0D structures like quantum dots all the three spatial directions are quantized. Hence the density of states for 0D structures is modified and expressed as

$$\rho(E)_{0D} = \sum_i 2\delta(E-E_i) \quad \text{.....(5)}$$

Where the summation is over all of the i quantum states.

The density of states for 3D, 2D, ID and 0D electron systems for one quantized level are shown in the Fig – 1.4(b)

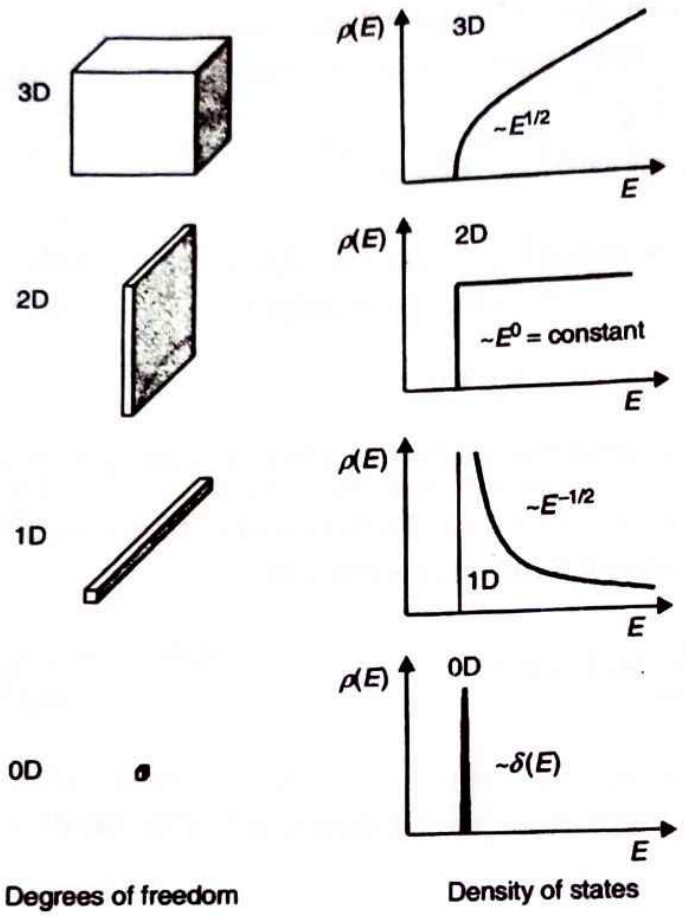


Fig.1.4(b) Density of states of 3D, 2D, 1D and 0D structures with the corresponding degrees freedom.

An electronic state can be occupied by an electron or unoccupied and the counting statistics of concentration of electrons in a band is based on

Number of electrons in a band = Number of states in the band

× probability of occupancy of that state by an electron

Now an energy states at energy E has a definite probability to be occupied by an electron given by the probability of occupancy f(E). This probability of occupancy f(E) is the main conclusion of the Fermi– Dirac statistics and f(E) is known as Fermi distribution function. Hence the number of electrons over the energy interval E– E +dE is found to be ρ (E) dE × f(E). Therefore the total number of electrons in a band is obtained by integrating over the top (E_t) to bottom E_0 of the band and is given by

$$n = \int_{E_b}^{E_t} \rho(E) f(E) dE \qquad .....(6)$$

The number of conduction electrons in the conduction band of a semiconductor at a temperature T is given by

$$n = \int_{Ec}^{\infty} \rho(E) f(E) dE \qquad .....(7)$$

The number of holes in the valence band at temperature T is given by

$$p = \int_{-\infty}^{E_v} \rho(E)[1 - f(E)] dE \qquad .....(8)$$

The fermi-Diral distribution f (E) applies to fermions, particles with half intiger spin which must obey the pauli exclusion principle. Each type of distribution function has a normalisation term multiplying the exponential in the denominator which may be temperature dependent For Fermi-Dirac distribution function that term s usually written as $e^{\frac{-E_F}{KT}}$ where E_F is the Fermi energy, K is the Biltzman constant and T is the absolute temperature.

The Fermi-Dirac distribution function is given by

$$f_{ED}(E) = \frac{1}{1+e^{\frac{E-E_F}{KT}}} \qquad .....(9)$$

where $f_{FD}(E)$ is the probability of a fermion with energy E and term 1 appears in the denominator due to the fact that particles are indistinguishable.

At T = 0K, $f_{FD}(E)1$ for $E < E_F$

and at T = 0K, $f_{FD}(E) = 0$ for $E > E_F$

We consider all the energy levels up to the Fermi energy are filled and no particle has a greater energy. This is wholly consistent with the Pauli exclusion principle where each quantum state can have only one particle. The temperature dependency of Fermi function is shown in the Fig.1.4(c). With the rise in temperature T, $f_{FD}(E)$ the step function smears out at higher temperatures.

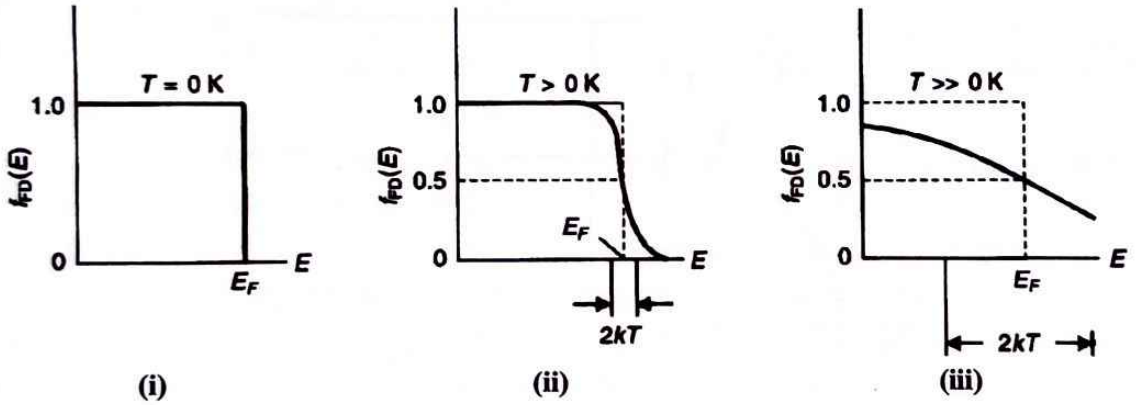


Fig.1.4(c) Temperature variations of Fermi-Dirac function.

At $T > 0$ and $E = E_F$, $f_{FD}(E) = \frac{1}{2}$

Hence Fermi energy is defined as that energy at T > 0 for which the probability of occupancy $f_{FD}(E)$ is equal to $\frac{1}{2}$.

For metals Fermi energy is defined as that energy for which at T = 0 all the energy levels below the conduction band are filled with electrons and all the energy levels above the conduction band are empty. Electrons are free to move into the empty states of conduction band with only a small electric field leading to high conductivity. At T > 0, electrons have a probability to be thermally excited from below the Fermi energy to above it. The band diagram of metals is shown in Fig 1.4(d).

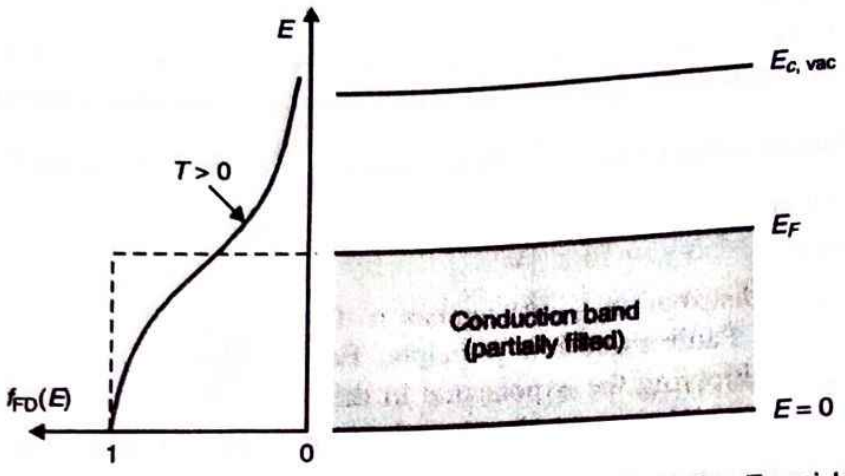


Fig. 1.4(d) Band diagram of metals. Electrons are occupied up to the Fermi level at $T = 0$ K.

For insulators the Fermi level lies at the mid point of the large (6 – 10eV) band gap as shown in the Fig – 1.4(e). At T = 0, valence band is filled with electons' and conduction band is empty, leading to zero conductivity. At T > 0, most of the valence electrons do not gain thermal energy to jump from valence band to conduction band, leading to poor conductivity.

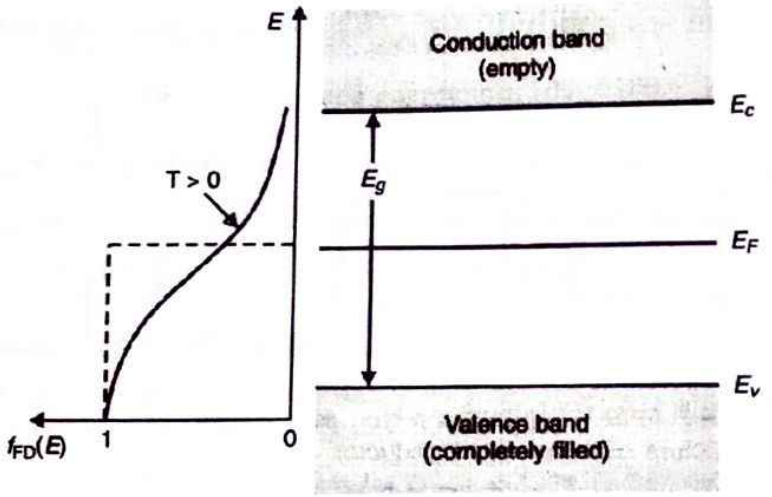


Fig. 1.4(e) Band diagram of insulators. Fermi energy lies in-between the forbidden gap, E_g

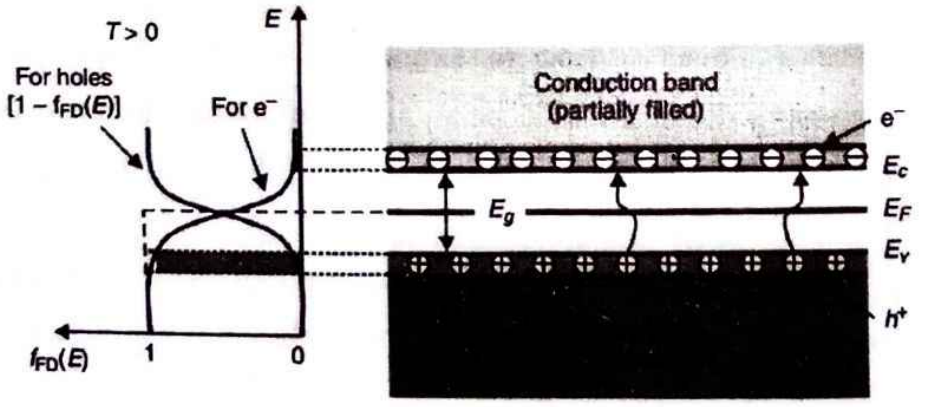


Fig. 1.4(f) Band diagram of intrinsic semiconductor. Fermi energy lies at the middle of the forbidden gap, E_g.

For instrinsic semiconductors, Fermi level lies at the middle of the band gap as shown in the Fig.1.4(f) At T = 0, valence band is completely filled and conduction band is empty, leading to zero conductivity. At T > 0 electrons in the valence band gain thermal energy and jump to conduction band leaving an empty state in the valence band called hole.Hence the conductivity of semiconductors increases with the increase in temperature.

For doped semiconductors the conductivity increases by adding a small amount of another metal called a dopant, in it. If the dopant is a donor them the dopant donates electrons to the semiconductor and makes n-type material. For example GrV Phospherous is used as donor type dopant in Gr IV silicon. Each P atom donates one electron which is weakly bound with donor energy level E_D just below the conduction band E_i . These electrons can easily be transferred to conduction band, leading to increase in electrical conductivity. The Fermi level E_F moves up towards E_C as shown in the Fig-1.4(g)

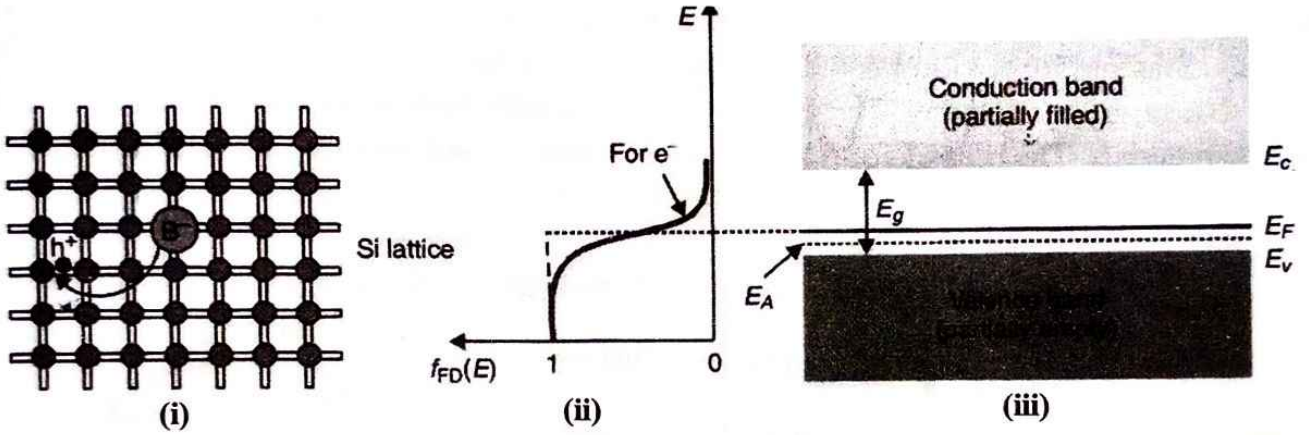


Fig.1.4(g) (i) Doping of B in Si lattice to get *p*-type conductivity, (ii) Fermi energy distribution, and (iii) band structure of *p*-type semiconductor.

For acceptor type doping the dopant accepts electron from the semiconductor and makes p – type material. For example Gr III boron is used as acceptor type dopant in Gr IV silicon. Each boron atom accepts one electrom from the semiconductor, creating an acceptor level E_A, just above the valence band edge E_v. The missing electron produces an extra hole within the valence band. These holes in the valence band, increases the conductivity of the material. The Fermi level E_F moves down towards E_v as shown in the Fig- 1.4(h)

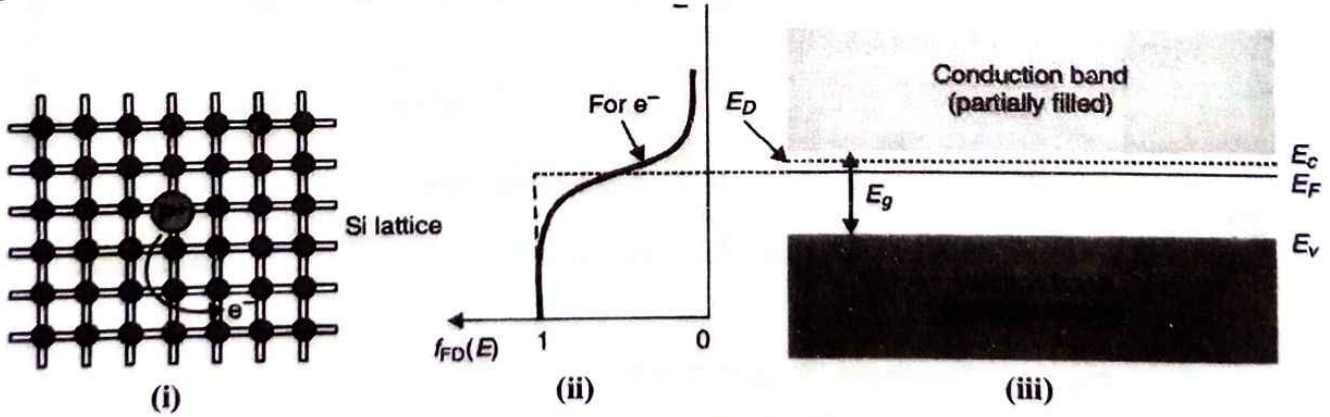


Fig.1.4(h) (i) Doping of P in Si lattice to get *n*-type conductivity, (ii) Fermi energy distribution, and (iii) band structure of *n*-type semiconductor.

1.5 SIZE-EFFECTS IN NANO SYSTEMS

There are many advantages of making things smaller. In modern semiconductor industry, miniaturization of devices often delivers more efficient performance. What would be the limits of miniaturization ? This is the main quistion. Theoretically, devices can be miniaturized to atomic level whose sizes can be changed from fraction of nanometer to few hundreds of nanometers. Nanotechnologe deals with these kinds of human designed working devices produced in a controlled and reproducible manner. The idea of miniaturization of the size-scale is interesting due to the fact that as size approaches the atomic scale the relevant physics associated with the systems changes from classical domain to quantum mechanical regime. These changes in the behaviours from classical to atomic scale via mesoscopic domain can be explained by modern quantum mechanical treatments. It must be noted that these changes from classical physics to quantum-mechanical nanphysics may mean that some existing devices will fail while the same changes can open up possibilites for new devices. Starting from a human hair to DNA structure the nature evolves itself from micro-scale to nano-scale structures. The modern world is now shifting its attention from micro devices to nanomaterials. The broad spectrum of the micro-regime and nano-regime is described in Fig 1.5(a). Consider the size effects in some smaller systems.

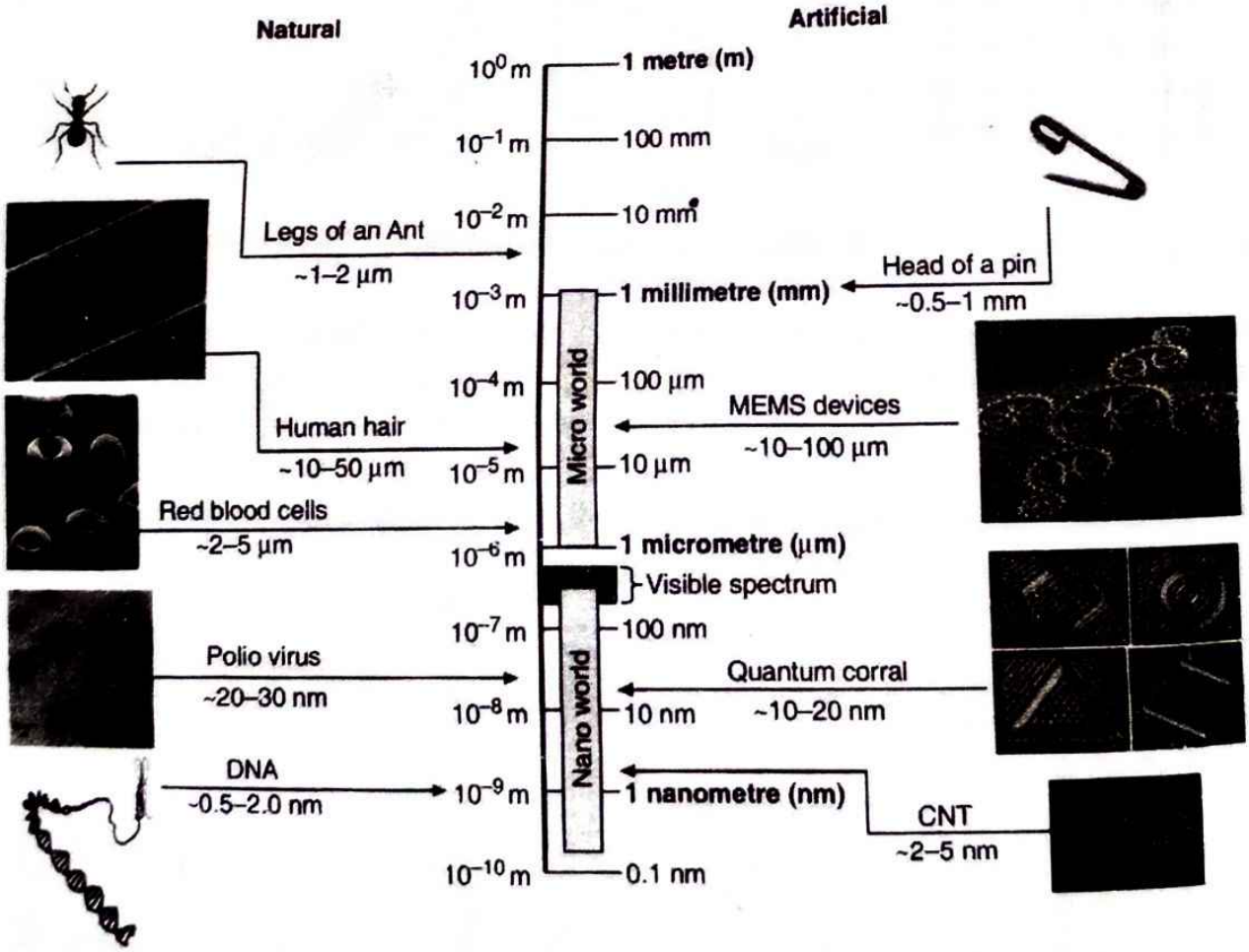


Fig.1.5(a) Description of nano-regime

1.5.1 - Response time increases for miniaturized simple pendulum

The resonant frequency of a simple pendulum is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{g}{\ell}} \qquad \text{.....(1)}$$

where g is the acceleration due to gravity and l is the length of the simple pendulum. This shows that a simple pendulum of 1μm length will generate a frequency of 1000Hz corresponding a time period of 1ms. Hence the miniature virsion of the simple pendulum has a much faster response time with respect to a normal simple pendulum which would have a resolution of 1s for a pendulum length of 1m.

1.5.2 – Thermal time constant decreases in smaller systems

Consider a hot body at T > 0K of heat capacity per volume C, connected to a cold body at T = 0K through a heat channel of length l, area of cross section 'a' and thermal heat capacity 'K' as shown in the Fig 1.5(b).

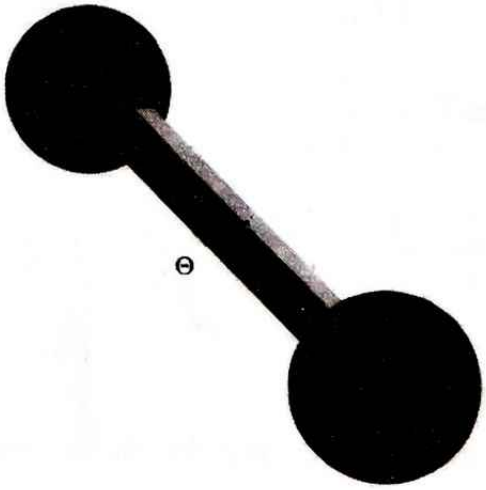


Fig. 1.5(b) : Heat transfer from a hot body to a cold body through a heat channel

The rate of flow of heat from hot body to cold body is given by

$$\frac{dQ}{dt} = \frac{KaT}{l} \qquad \text{.....(1)}$$

At steady state this rate of flow of heat is equal to the rate of loss of heat from the hot body

$$\therefore \frac{dQ}{dt} = -CV\frac{dT}{dt} \qquad \text{.....(2)}$$

wher V is the volume of the hot body and the negative sign indicates the loss of heat from the hot body.

Equating eq^n (1) and eqn (2) we get

$$\frac{KaT}{\ell} = -CV\frac{dT}{dt}$$

$$\text{or } \frac{dT}{T} = -\left(\frac{ka}{CV\ell}\right)dt \qquad \text{.....(3)}$$

$$\text{now } \frac{CV\ell}{ka} = \tau \qquad \text{.....(4)}$$

where τ is called the thermal time constant which has the dimension of $[L^2]$ under isotropic environment.

Using eq^n (3) we get

$$\frac{dT}{T} = -\frac{1}{\tau}dt$$

Integrating both the sides

$$\int_{T_o}^{T} \frac{dT}{T} = -\int_{o}^{t} \frac{1}{\tau}dt$$

$$\text{or } \left[\ln T\right]_{T_o}^{T} = -\left[\frac{t}{\tau}\right]_{o}^{t}$$

$$\text{or } \ln T - \ln T_o = -\frac{t}{\tau}$$

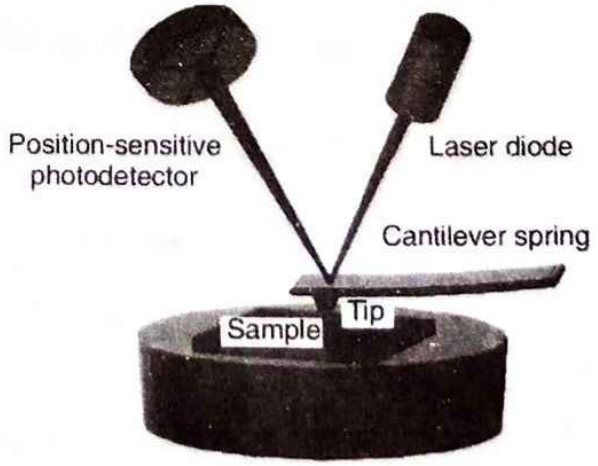
$$\text{or } \ln\left(\frac{T}{T_o}\right) = -\frac{t}{\tau} \text{ or } \left(\frac{T}{T_o}\right) = e^{\frac{-t}{\tau}}$$

$$\text{or } T = T_o e^{\frac{-t}{\tau}} \qquad .....(5)$$

From equation (4) it is clear that the thermal time constant strongly decreases with the decrease in size of the system.

This Phenomenon is used for data storage system where the data bits are recorded with a resistively heated AFM tip and are detected by the integrated piezoelectric PZT senior. This system consumes less power and responds much faster. The image of a AFM tip and its working principle are shown in the Fig-1.5(c)

(i)



(ii)

Fig. 1.4(c) (i) SEM image of AFM tip, and (ii) schematic diagram of the working principle of AFM.

1.5.3 – Disappearance of friction in highly symmetric molecular systems :

According to Eric Drexler, the viscous and frictional forces are assumed to be zero in molecular-scale systems. Theoretical modelling shows that the self-alignment of the nanometer-scale wheels and axles in vaccum leads to absolute zero space for any fluid in the interface between the surfaces. Hence these moving parts will no longer experience any fluid viscous forces between them. Howsever these moving parts may encounter some frictional forces if any at a much lower level than ordinary mechanical frictional forces in these macroscoping moving parts. For example in nested carbon nanotubes which are rolled sheets of graphite as shown in Fig 1.5(d). These nanatubes have no dangling bonds perpendicular to their surfaces and there are no molecules between the surfaces of two adjacent tubes and hence the medium between the very closely spaced moving parts is vaccum. Therefore the motion between two neighbouring carbon nanotubes is almost frictionless.

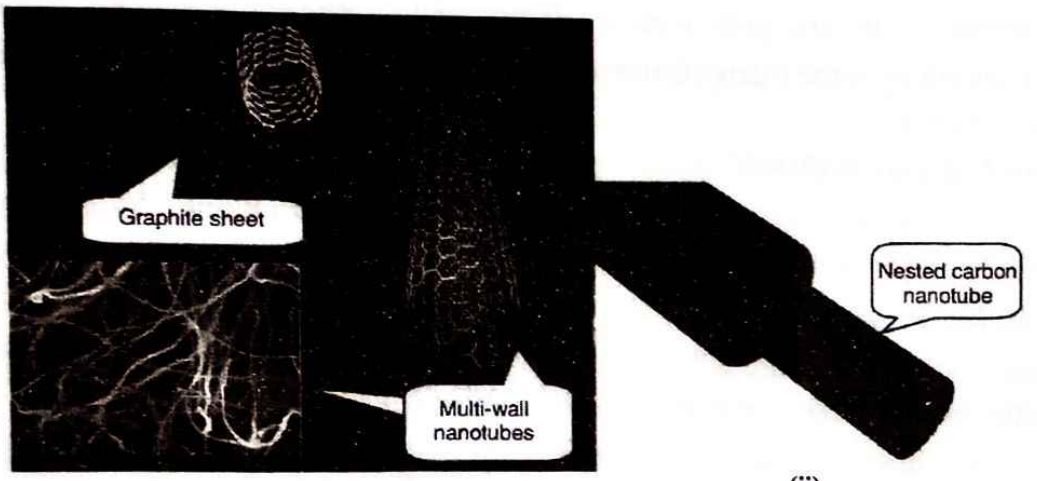


Fig.1.5(d) Schematic representation of **(i)** multi-wall carbon nanotubes formed from graphite sheets, and **(ii)** computer generated model of nested carbon nanotube.

The molecular bearing in biological rotary motors is an another example of frictionless motion. In biological rotary motors the molecular bearing rotates flagella to move cells in liquid. The flagellum is attached to a shaft, which rotates freely in a molecular structure. The rotation transmits torque and power and the motor operates continuously over the life of the cell which suggests a frictionless molecular bearing Fig-1.5(e) shows the schematic representation of E-coli bacterial flagella rotary motor.

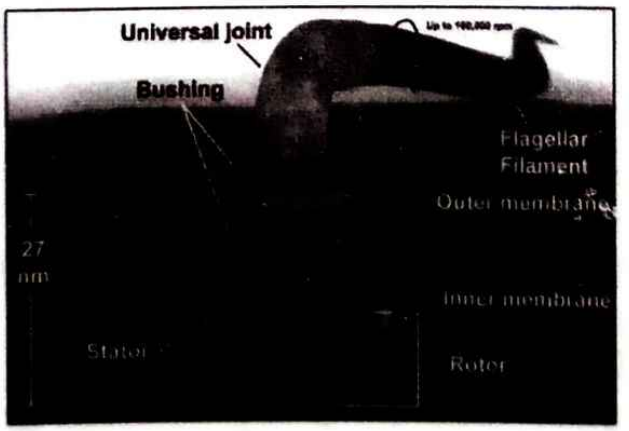


Fig. 1.5(e) Schematic representation of E-coli flagelta rotary motor

SUMMARY

- Nano refers to 10^{-9} and it can be ascribed to any unit of measurement.
- One nanometre means 10^{-9} metre
- Nanoscience is the study nano-structures and nano-materials.
- In nano regime the properties of structures are quite different as compared to their bulk structures.
- Nano-structures are the structures on the scale of nanometres.
- The principles of nano-science are now used by scientists and engineers from various disciplines like physics, chemistry, biology and material science for applications in energy, medicine, computing and data storage.
- Nano-science is an emerging area of a diverse field with very wide applications.
- Nano-technology is the manipulation of matter with at least one dimension in the range 1 to 100 nanometres.
- Nano-technology deals with both natural and artificial structures on the nanometre scale.
- Nano-materials lie in the physical regime between bulk macroscopic materials and the molecular compounds.
- Nano-technology and nano-science focus mostly on nanometre sized crystalline solids.
- The most notable change is the increase in surface area to volume ratio of the nano-materials over the bulk materials.
- The increase in surface to volume ratio for the nano-materials, is due to the fact that in nano-regime upto 50% of the atoms lie at the surface of the nano-structure.
- the surface is potentially important in dictating the optical and electrical properties of the material in the nano-regime.
- The increase in surface area is important in applications where S/V ratio plays a vital role, such as in photovoltaics and in catalysis.
- The surface is potentially important in dictating the optical and electrical properties of the material in the nano-regime.
- Every property of a material has a critical length associated with it.
- The critical length for the resistance of the material, is the scattering length which is the average distance travelled by an electron before it is scattered from positive ion cores in the lattice.
- The size dependent properties of solids such as electronic structure and mechanical properties change if particles become smaller than the critical size.
- The relevant length scales in physics are actually relative to the natural electron or hole length scales in the parent bulk material.
- A nano-material is in the quantum confinement regime if its size is less than the corresponding de Broglie wavelength of an electron or hole.

- A nano-material is quantum confined because its size is less than the correponding exciton Bohr radius.
- Bohr radius of an electron is given by $r_0 = \frac{4\pi \epsilon_0 \hbar^2}{m e^2}$
- An excition is the bound electron-hole pair in a semiconductor.
- Hence exciton Bohr radius is the distance between electron and hole in this pair.
- The exciton Bohr radius is given by $r_e = \frac{4\pi \epsilon_0 \epsilon_r \hbar^2}{m_{eff} e^2}$

  where, m_{eff} is effective mass of exciton and is given by $m_{eff} = \frac{m_e m_h}{m_e + m_h}$

  m_e = effective mass of electron.

  m_h = effective mass of hole
- Zero dimensional (0D) nano-structured materials are the materials in which nanoparticles are isolated from each other.
- Nanodots or quantum dots and magnetic quantum dots are zero dimensional (0D) nano-structured materials.
- The Degree of Freedom of 0D Nano-structured materials is zero :
- One dimensional (1D) nano-structured materials are materials with length from 100 nonometre to tens of microns.
- Nanorods, nanotubes and nanowires are 1D nano-structured materials.
- The degree of freedom of 1D nano-structured materials is one.
- Two dimensional (2D) nano-structured materials are materials with nanometre thickness.
- These materials include nanosheets, nanoribbons, nanomehses, graphene coats, and films.
- The degree of freedom of 2D nano-materials is two.
- Three dimensional (3D) Nano-structured materials are bulk materials.
- These materials include powder, fibrous, multilayer and polycrystalline materials.
- The degree of freedom of 3D nano-structured materials is three and they are not confined at all.
- Nanodots are zero dimensional nano-structures in which there is confinement along all the three directions. Nanodots are also known as quantum dots.
- Nanodot could potentially store over one hundred times more data than the present hard drives. Nanodots can be considered as tiny magnets which can switch polarity to present a binary digit.
- Thin films are two dimensional nano-structures in which there is confinement along one direction.

- Thin films are created through a process called deposition. Deposition is a thin film coating process which is achieved by modifying the four states of matter such as solid, liquid, gas and plasma.
- Ferromagnetic and ferro-electric thin films are used as computer memory.
- Thin film technology is used in the manufacturing of reflective or antireflective or self-cleaning glass.
- Nanowires are one dimensional nano-structures in which there is confinement along two directions.
- Nanowires are also known as quantum wires.
- Nanorods are one dimensional nano-structures in which there is confinement along two directions.
- Nanorods can synthesized from metal, or semiconducting materials.
- Nanorods are produced by direct chemical synthesis.
- Nanorods along with other metal nano-particles also act as theragnostic agents. Nanorods are used as cancer therapeutics because they absorb heat in the IR region and generate heat when excited with IR light.
- Nanorods are used in the treatment of tumors.
- In crystalline solids the electronic energy levels are different from that of a single atom.
- The potential characterization of the crystalline structure is a periodic function in space whose value at any point is the result of contribution of each atom.
- The inner-shell electrons of the individual atoms in crystalline solids are not affected by the neighbouring atoms but the energy levels of the outer shell electrons are changed since these electrons are shared by all the neighbouring atoms.
- The electronic band structures are usually associated with crystalline materials. The quasi crystalline and amorphous solids may also exhibit band structures.
- Electrical conduction is produced within a material due to the motion of charge carriers under the influence of an applied electric field.
- A material is a conductor if it contains a large umber of free charge carriers.
- In metals the valence electrons from the atoms form a cloud of electrons due to the nature of metallic bonding.
- A material with a very poor conductivity is called an insulator or non-conductor. A material having conductivity, between conductors and insulators, is called semiconductors, In general, insulators and semiconductors do not have metallic bonding.
- According to electrical conductivity materails can be classified into conductors, semiconductors and insulators.

- The metals are excellent conductors, insulators are poor conducto of electrons and semiconductors lie between conductors and insulators.
- According to band structure materials can also classified into three categories, e.g conductors, semiconductor and insulators.
- Metals have partially filled conduction band and under the influence of an external electric field the electrons gain additional energy and move to higher states and constitute electric current.
- In metals the conduction band and the valence band overlap with each other.In insulators the energy gap (E_g) is very large ($E_g \simeq 6eV$).
- The insulators are poor conductors of electrons.
- In semiconductors, the energy gap (E_g) is very small ($E_g \simeq leV$).
- The empty states in the valence band are known as holes which also act as the carrier of electricity.
- The conductivity of semiconductors increases with the increase in temperature.
- The energy and volume density of electronic energy levels in a crystalline solid, change across the energy band.
- The number of electronic energy levels per unit volume over the energy interval $E \sim E + dE$ are known as the density of states (DOS) and defined as $\rho(E)\,dE$ where $\rho(E)$ is the density of states.

- The density of states for a 3D crystal is expressed as $\rho(E)_{3D} = \frac{1}{2\pi^2}\left(\frac{2m'}{\hbar^2}\right)^{\frac{3}{2}}(E-E_p)^{\frac{1}{2}}$

- The density of states for 2D structure is modified and can be expressed as

$$\rho(E)_{2D} = \frac{m'}{\pi\hbar^2}\sum_i H(E-E_i)$$

- The density of states for ID structure is expressed as $\rho_{(E)_{ID}} = \frac{1}{\pi}\left(\frac{2m'}{\hbar^2}\right)^{\frac{1}{2}}\sum_i \frac{n_i H(E-E_i)}{(E-E_i)^{\frac{1}{2}}}$

- The density of states for 0D structures is modified and expressed as

$$\rho(E)_{0D} = \sum_i 2\delta(E-E_i)$$

- The number of conduction electrons in the conduction band of a semiconductor at a temperature T is given by $n = \int_{E_c}^{\infty} \rho(E) f(E)\,dE$

- The number of holes in the valence band at temperature T is given by

$$p = \int_{-\infty}^{E_v} \rho(E)\left[1 - f(E)\right] dE$$

- The Fermi-Dirac distribution function is given by $f_{ED}(E) = \frac{1}{1 + e^{\frac{E - E_F}{KT}}}$
- For metals Fermi energy is defined as that energy for which at T = 0 all the energy levels below the conduction band are filled with electrons and all the energy levels above the conduction band are empty.
- For insulators the Fermi level lies at the mid point of the large (6 – 10eV) band gap
- For instrinsic semiconductors, Fermi level lies at the middle of the band gap
- The conductivity of semiconductors increases with the increase in temperature.
- If the dopant is a donor them the dopant donates electrons to the semiconductor and makes n-type material.
- For acceptor type doping the dopant accepts electron from the semiconductor and makes p – type material.
- In modern semiconductor industry, miniaturization of devices often delivers more efficient performance.
- Devices can be miniaturized to atomic level whose sizes can be changed from fraction of nanometer to few hundreds of nanometers.
- Nanotechnologe deals with these kinds of human designed working devices produced in a controlled and reproducible manner.
- As size approaches the atomic scale the relevant physics associated with the systems changes from classical domain to quantum mechanical regime.
- The modern world is now shifting its attention from micro devices to nanomaterials.
- The miniature virsion of the simple pendulum has a much faster response time with respect to a normal simple pendulum
- The thermal time constant strongly decreases with the decrease in size of the system.N
- The motion between two neighbouring carbon nanotubes is almost frictionless.

QUESTIONS

Long Answer Type Questions :

1. Describe length scales in physics.
2. What do you mean by nanostructured materials ? Explain 0D, 1D, 2D and 3D nanostructures
3. Write short notes on
   (a) Nanodots
   (b) Nanorods
   (c) Nanowires
   (d) Thin films
4. Describe the band structure of materials at nanoscale.
5. Describe the density of states of materials at nanoscale.
6. Discuss about the size effects in nano systems.

Very Short Answer Type Questions :

1. What refers to nano ?
2. What do you mean by Nano science ?
3. What is the wide of a single strand of DNA ?
4. What are nano-structures ?
5. What do you mean by Nano-technology ?
6. Which technology is capable of manipulating single atoms and molecules ?
7. What are the different fields of applications of Nano-technology ?
8. Which materials lie in the physical regime between bulk macroscopic materials and molecular compounds ?
9. Write the names of three categories of solids.
10. Which properties of the material are changed upon reaching nano regime ?
11. What is the cause of the increase in surface to volume ratio for the nano-materials ?
12. Write examples where the properties of materials change while going from bulk to nanosize ?
13. What is critical length ?
14. What is scattering length ?
15. What are size dependent properties of solids ?
16. When the size dependent properties of solids change ?
17. When the nano-material is in the quantum confinement regime ?
18. What is Bohr radius ?
19. What is an exciton ?
20. What is exciton Bohr radius ?
21. What is the degree of freedom of zero dimensional nano-structured materials ?
22. Write examples of OD nano-materials.

23. What are OD nano-structured materials ?
24. What are one dimensional nano-structured materials ?
25. What is the degree of freedom of one dimensional nano-structured materials ?
26. What are two dimensional nano-structured materials ?
27. What is the degree of freedom of 2D NSM ?
28. Write examples of 2D NSM.
29. What are 3D NSMs ?
30. What is the degree of freedom of 3D NSM ?
31. Write examples of 3D NSM.
32. What are quantum dots ?
33. What are thin films ?
34. What are nano-wires ?
35. What are nano-rods ?
36. What are thin films ?
37. Why nanorods are used as cancer therapeutics ?
38. Write an expression for the density of states for 3D nano-crystal.
39. Write an expression for density of states for 2D nano-structure.
40. Write an expression for density of states for 1D nano-structure.
41. Write an expression for density of states for OD nano-crystal.
42. Explain how response time increases for miniaturized simple pendulum ?
43. Thermal time constant decreases in smaller systems. Explain
44. Disappearance of friction in highly symmetric molecular systems. Explain
45. How the band structure of a solid crystal is obtained ?
46. What is valence band ?
47. What is conduction band ?
48. What is energy gap ?
49. What are metals ?
50. What are insulators ?
51. What are semiconductors ?
52. Define density of states.
53. Explain the band diagram of metals.
54. Explain the band diagram of insulators.
55. Explain the band diagram of intrinsic semiconductors.
56. Explain the band diagram of p-type semiconductors.
57. Explain the band diagram of n-type semiconductors.

CHAPTER 2

QUANTUM CONFINEMENT

LEARNING OBJECTIVES

- Introduction, Applications of schrodinger equation.
- Quntum confinement of carriers in nanostructures and its consequences.

2.0 INTRODUCTION

Quantum confinement is the change of electronic and optical properties when the material is of sufficiently small size i.e 10 nanometres or less. The bandgap increases with the decrease in the size of the nanosructure. Specifically the phenomenon results from electrons and holes being squeezed into a dimension that approaches a critical quantum measurement called the exciton Bohr radius.Since the bandgap and wavelength are inversely related to each other, the wavelength decreases with the decrease in size of the nanostructure. For example the emission of blue radiation from nano particle and the emission of red radiation from bulk material.

2.1. APPLICATIONS OF SCHRODINGER EQUATION

The time-dependent Schrodinge equation in 1D is given by

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_{(x,t)} + U_{(x,t)}\Psi_{(x,t)} = i\hbar\frac{\partial}{\partial t}\Psi_{(x,t)} \qquad \text{.....(1)}$$

where $\hbar(=\frac{h}{2\pi})$ = reduced form of Planck's constant

m = the mass,

$\Psi_{(x,t)}$ = wave function

and $U_{(x,t)}$ = potential energy

The time – dependent Schrodinger equation in 3D is given by

$$[-\frac{\hbar^2}{2m}\nabla^2 + U_{(\vec{r},t)} - i\hbar\frac{\partial}{\partial t}]\psi_{(\vec{r},t)} = 0 \quad \text{.....(2)}$$

The time - independent Schrodinger equation in 1 D is given by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{(x)} + U_{(x)}\psi_{(x)} = E\psi_{(x)} \quad \text{.....(3)}$$

where E is the total energy

The time-independent schrodinger equation in 3D is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{(\vec{r})} + U_{(\vec{r})}\psi_{(\vec{r})} = E\psi_{(\vec{r})} \quad \text{.....(4)}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and $\vec{r}$ is the position vector

2.1.1 Infinite Potential well

Consider a particle confined in 1D according to the following potential distribution.

$U = 0$ for $0 < x < L$

$U \to \infty$ for $x \geq L$ and $x \leq 0$

This can be described in the Fig–2.1.1

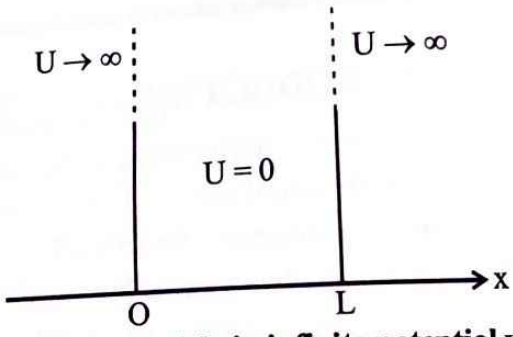


Fig. 2.1.1(a) : Particle in infinite potential well

This indicates that the probability of finding the particle outside the well is zero

The particle will require infinity energy to come out of the well.

$\therefore \psi_{(x)} = 0$ for $x \leq 0$ and $x \geq L$

$\psi_{(x)}$ = finite inside the well

According to time – independent Schrodinger equation in 1D

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{(x)} + U_{(x)}\psi_{(x)} = E\psi_{(x)}$$

Inside the infinite potential well the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{(x)} = E\psi_{(x)}$$

$$\text{or } \frac{d^2}{dx^2}\psi_{(x)} = -\frac{2m}{\hbar^2}E\psi_{(x)}$$

$$\text{or } \frac{d^2}{dx^2}\psi_{(x)} + \frac{2mE}{\hbar^2}\psi_{(x)} = 0 \qquad \ldots\ldots (1)$$

The general solution of this second-order linear differential equation will be

$$\psi_{(x)} = Ae^{ikx} + Be^{-ikm} \qquad \ldots\ldots (2)$$

Where i^2 is -1, A and B are constants

$$\text{and } k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \ldots\ldots (3)$$

Consider the following boundary conditions

$$\psi_{(o)} = \psi_{(L)} = 0 \qquad \ldots\ldots (4)$$

$$\frac{d}{dx}(\psi_{(x)}|_{x=o}) = \frac{d}{dx}(\psi_{(x)}|_{x=L}) = 0 \qquad \ldots\ldots (5)$$

Using equation (2) We get

$\psi_{(x)} = A(\cos kx + i\sin kx) + B(\cos kx - i\sin kx)$

$\psi_{(x)} = A\cos kx + iA\sin kx + B\cos kx - iB\sin kx$

Again using equation (2) we get

$\psi_0 = 0 = Ae^{o} + Be^{-o}$

$\Rightarrow A + B = 0$

$\Rightarrow A = -B \qquad \ldots\ldots (7)$

Using equation (6) we get

$\psi_{(x)} = A\cos kx + iA\sin kx - A\cos kx + iA\sin kx$

$\psi_{(x)} = 2iA\sin kx \qquad \ldots\ldots (8)$

Now $\psi_{(L)} = 0 = 2\,iA\sin kL$

$\Rightarrow \sin kL = 0$

$\Rightarrow \sin kL = \sin N\pi$

where n = 1, 2, 3 .....

or $kL = n\pi$

$$\text{or } k = \frac{n\pi}{L} \qquad \ldots\ldots (9)$$

Using equation (3) we get

$$E = \frac{k^2\hbar^2}{2m}$$

$$E_n = \left(\frac{n\pi}{L}\right)^2 \left(\frac{h^2}{4\pi^2}\right)\left(\frac{1}{2m}\right)$$

$$\Rightarrow E_n = \frac{n^2h^2}{8mL^2} \qquad \text{..... (10)}$$

where n = 1, 2, 3 .....

Using equation (8) we can write

$$\psi_n(x) = A_1 \sin\left(\frac{n\pi x}{L}\right) \qquad \text{..... (11)}$$

where n = 1,2, 3 .....

and A_1 = normalization constant.

$$A_1 = 2iA \qquad \text{..... (12)}$$

The normalization constant can be determined by the probability of finding the particle inside the potential well as unity

$$\therefore \int_0^L |\psi_n(x)|^2 \, dx = 1$$

$$\text{or } \int_0^L \left| A_1 \sin\frac{n\pi x}{L} \right|^2 dx = 1$$

$$\text{or } A_1^2 \int_0^L \sin^2\frac{n\pi x}{L} dx = 1$$

$$\text{or } \frac{A_1^2}{2} \int_0^L \left(1 - \cos\frac{2\pi n x}{L}\right) dx = 1$$

$$\text{or } \frac{A_1^2}{2}\left[x - \frac{\sin\frac{2\pi n x}{L}}{\frac{2\pi n}{L}}\right]_0^L = 1$$

$$\text{or } \frac{A_1^2}{2}\left[L-\frac{L\sin 2\pi n}{2\pi n}-0+0\right]=1$$

$$\text{or } \frac{A_1^2}{2}(L-0)=1$$

$$\text{or } \frac{A_1^2 L}{2}=1$$

$$\text{or } A_1^2=\frac{2}{L}$$

$$\text{or } A_1=\sqrt{\frac{2}{L}} \qquad \text{..... (13)}$$

The normalized wavefunction $\psi_n(x)$ is known as eigenfunction and is given by

$$\psi_n(x)=\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\frac{n\pi x}{L} \qquad \text{..... (14)}$$

All $\psi_n(x)$ for $n=1,2,3$ ..... constitute the eigenfunctions of the system. The energies of the system E_n for 1,2 , 3.... are known as eigenenergies of the system.

The behaviour of a trapped electron inside an infinite potential well can be explained pictorially in the Fig-2.1.1(b) It is clear from equation (10) and equation (14) that both eignenegy E_n and eignfunction $\psi_n(x)$ are dependent on the quantum number n.

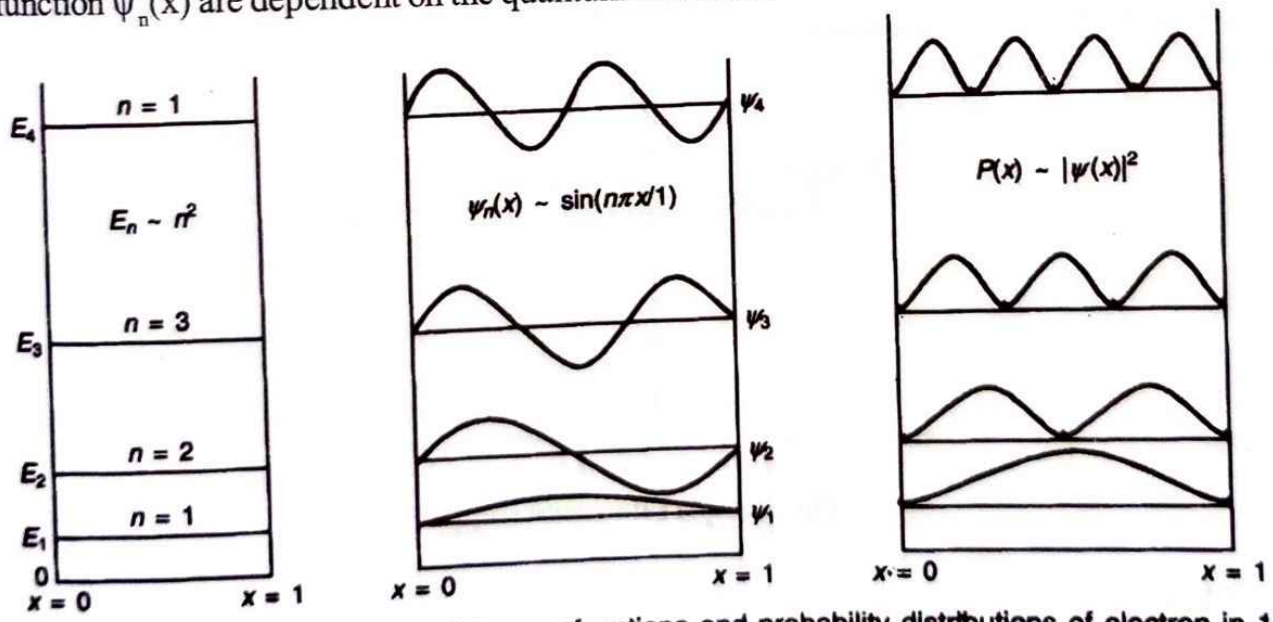


Fig.2.1.1(b) Energy distribution, possible wavefunctions and probability distributions of electron in 1D infinite potential well.

The energy is quantized and can take only finite values and it is directly proportional to n^2. Hence the lowest energy corresponds to n=1. This lowest energy is known as ground state energy which is the minimum energy the electron can possesses. According to the uncertainty principle the lowest energy of the electron cannot be zero. It must have a certain momentum, so also the kinetic energy is in the lowest state even though the potential energy is zero. This example of infinite quantum well problem illustrates the nanophysical behaviour that there are discrete allowed energy levels and wavefunctions do not locate an electron and they only provide the statements on the probability of finding an electron in the given range.

Two non-interacting particles simultaneously situated in the 1D potential well can be described by a two-particle wavefunction. If the particles are situated in two quantum states n_1 and n_2 then the two particle wavefunction can be written as

$$\psi_{n_1n_2}(x_1x_2) = A^2 \sin\left(\frac{n_1\pi x_1}{l}\right)\sin\left(\frac{n_2\pi x_2}{l}\right)$$

$$= \psi_{n_1}(x_1)\psi_{n_2}(x_2) \qquad \ldots\ldots (15)$$

The corresponding probability density can be written as

$$P_{n_1n_2}(x_1x_2) = \psi^*_{n_1n_2}(x_1, x_2)\, \psi_{n_1n_2}(x_1, x_2) \qquad \ldots\ldots (16)$$

2.1.2. Potential step

Consider a particle moving along positive x – axis towards a finite potential step as shown in Fig 2.1.2(a).

The potential function of a potential step can be defind as

$V_{(x)f} = 0$ for $x < 0$ in region I

$V_{(x)} = V_0$ for $x \geq 0$ in region II

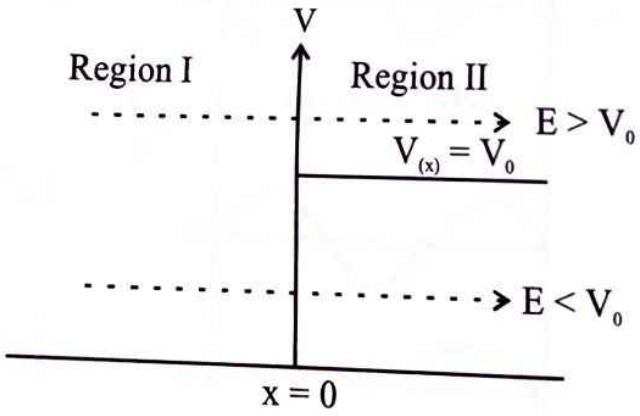


Fig. 2.1.2(a) : Potential step

Case-I : $E > V_0$

If the incoming particle has energy more than the potential step then the schrodinger equation in region 1 is given by

$$\frac{d^2\psi_{(x)}}{dx^2} + k_1^2\psi(x) = 0 \qquad \ldots\ldots (1)$$

$$\text{where } k_1^2 = \frac{2mE}{\hbar^2}$$

The Schrodinger equation in region II is given by

$$\frac{d^2\psi_{(x)}}{dx^2} + k_2^2\psi(x) = 0 \qquad \ldots\ldots (2)$$

$$\text{where } k_2^2 = \frac{2m(E - V_o)}{\hbar^2}$$

The solution of equation (1) for $x < 0$ in region I is

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad \ldots\ldots (3)$$

where A and B are arbitrary Constants. Physically A denotes the amplitude of incident wave moving along positive x-direction and B denotes the amplitude of reflected wave moving along negative x-direction in region 1.

$$\psi_{in}(x) = Ae^{ik_1x}$$

$$\psi_{ref}(x) = Be^{-ik_1x}$$

The solution of equation (2) for $x \leq 0$ in region II is

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \qquad \ldots\ldots (4)$$

Where C and D are arbitrary constants. Physically C denotes the amplitude of transmitted wave moving along positive x-axis in region II. Since no particles are incident from right $D = 0$,

$$\therefore \psi_{tr}(x) = Ce^{ik_2x}$$

According to boundary condition of continuity for $\psi_{(x)}$ at $x = 0$

$$\psi_1(x) = \psi_2(x)$$

$$\Rightarrow A + B = C \qquad \ldots\ldots (5)$$

According to boundary conditions of continuity for $\frac{\partial\psi}{\partial x}$ at $x = 0$

$$\frac{\partial\psi_1}{\partial x} = \frac{\partial\psi_2}{\partial x}$$

$$\frac{\partial}{\partial x}\left[Ae^{ik_1x} + Be^{-ik_1x}\right] = \frac{\partial}{\partial x}\left[Ce^{ik_2x}\right]$$

$$\Rightarrow ik_1Ae^{ik_1x} - ik_1Be^{-ik_1x} = ik_2Ce^{ik_2x}$$

At $x = 0$ we get

$$ik_1(A-B) = ik_2C$$

$$\text{or } A-B = \frac{k_2}{k_1}C \qquad \ldots\ldots (6)$$

Adding equations (5) and (6) we get

$$2A = C\left(1+\frac{k_2}{k_1}\right)$$

$$\text{or } 2A = C\left(\frac{k_1+k_2}{k_1}\right)$$

$$\text{or } \frac{C}{A} = \frac{2k_1}{k_1+k_2} \qquad \ldots\ldots (7)$$

$$\Rightarrow C = \frac{2k_1A}{k_1+k_2}$$

Using equation (6) we get

$$A-B = \frac{k_2}{k_1}\left(\frac{2k_1A}{k_1+k_2}\right)$$

$$A-B = \frac{2k_2A}{k_1+k_2}$$

$$\text{or } A - \frac{2k_2A}{k_1+k_2} = B$$

$$\text{or } A\left(1-\frac{2k_2}{k_1+k_2}\right) = B$$

$$\text{or } A\left(\frac{k_1+k_2-2k_2}{k_1+k_2}\right) = B$$

$$\text{or } A\left(\frac{k_1-k_2}{k_1+k_2}\right) = B$$

$$\text{or } \frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \qquad \text{.....(8)}$$

The transmission coefficient is defined as the probability ratio of transmitted particle wave with respect to the probability ratio of incident particle wave

$$\therefore T = \frac{k_2}{k_1}\left|\frac{C}{A}\right|^2 = \frac{k_2}{k_1}\left(\frac{2k_1}{k_1 + k_2}\right)^2$$

$$\text{or } T = \frac{4k_1k_2}{(k + k_2)} \qquad \text{..... (9)}$$

The reflection coefficient is defined as the probability ratio of reflected particle wave with respecto to protability ratio of incident particle wave.

$$\therefore R = \frac{k_1}{k_1}\left|\frac{B}{A}\right|^2$$

$$\text{or } R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \qquad \text{..... (10)}$$

It was found that

$$R + T = 1 \qquad \text{..... (11)}$$

This means the total probability is always unity. The expressions (9) and (10) are similar to the laws of reflection and transmission of light between the two media of different refractive indices. In case of particle waves the expressions physically mean that a quantum particle will be partially reflected even if it has enough energy propagate past the step potential Vo. This condition illustrates the nanophysical behaviour of quantum world whcih is quite different from the classical concept.

Case 11: $E < V_o$

If the incoming particle has energy less than the step potential then the Schrodinger equation in region I is give by

$$\frac{d^2\psi(x)}{dx^2} + k_1^2\psi(x) = 0 \qquad \text{..... (12)}$$

$$\text{where } k_1^2 = \frac{2mE}{\hbar^2}$$

The schrodinger equation in region II is given by

$$\frac{d^2\psi(x)}{dx^2} - k_3^2\psi(x) = 0 \qquad \text{..... (13)}$$

where $k_3^2 = \frac{2m(V_o - E)}{\hbar^2} = -k_2^2$

The solution to equation (12) for $x < 0$ in region I is given by

$$\psi_1(x) = A_1 e^{ik_1 x} + B_1 e^{-ik_1 x} \quad \ldots\ldots (14)$$

The solution to equation (13) for $x \geq 0$ in region II is given by

$$\psi_2(x) = C_1 e^{-k_3 x} + D_1 e^{k_3 x} \quad \ldots\ldots (15)$$

Where A,B, C and D are arbitrary constents.

It is clear that as $x \to \infty, e^{K_2 x} \to \infty$. Hence D_1 must be Zero to prevent the particles from unphysically collecting at large positive x.

According to boundary condition of continuity for $\psi(x)$ at $x = 0$.

$$\psi_1(x) = \psi_2(x) \quad \ldots\ldots (16)$$

$$\Rightarrow A_1 + B_1 = C_1$$

According to boundary condition of continuity for $\frac{\partial \psi}{\partial x}$ at $x = 0$

$$\frac{\partial \psi_1}{\partial x} = \frac{\partial \Psi_2}{\partial x}$$

$$\frac{\partial}{\partial x}\left[A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}\right] = \frac{\partial}{\partial x}\left[C_1 e^{-k_3 x}\right]$$

$$\Rightarrow ik_1 A e^{ik_1 x} - ik_1 B_1 e^{-ik_1 x} = -k_3 C_1 e^{-k_3 x}$$

At $x = 0$ we get

$$ik_1(A_1 - B_1) = -k_3 C_1$$

$$\text{or } A_1 - B_1 = \frac{-k_3}{ik_1} C_1$$

$$\text{or } A_1 - B_1 = \frac{ik_3}{k_1} C_1 \quad \ldots\ldots (17)$$

Adding equation (16) and (17) we get

$$2A_1 = \left(1 + \frac{ik_3}{k_1}\right) C_1$$

$$2A_1 = \left(\frac{k_1 + ik_3}{k_1}\right) C_1$$

$$\frac{C_1}{A_1} = \frac{2k_1}{k_1 + ik_3} \qquad \text{..... (18)}$$

$$\Rightarrow C_1 = \left(\frac{2k_1}{k_1 + ik_3}\right) A_1$$

Using equation (16) we get

$$A_1 + B_1 = \left(\frac{2k_1}{k_1 + ik_3}\right) A_1$$

$$\text{or } B_1 = \left(\frac{2k_1}{k_1 + ik_3}\right) A_1 - A_1$$

$$\text{or } B_1 = \left[\frac{2k_1}{k_1 + ik_3} - 1\right] A_1$$

$$\text{or } B_1 = \left[\frac{2k_1 - k_1 - ik_3}{k_1 + ik_3}\right] A_1$$

$$\text{or } \frac{B_1}{A_1} = \frac{k_1 - ik_3}{k_1 + ik_3} \qquad \text{..... (19)}$$

The reflection coefficient is given by

$$R = \frac{k_1}{k_1}\left|\frac{B_1}{A_1}\right|^2$$

$$\text{or } R = \left|\frac{k_1 - ik_3}{k_1 + ik_3}\right|^2 = 1 \qquad \text{..... (20)}$$

The solution in Region II is an exponentially decaying function and this function is not automatically zero in the region of negative energy.

Now using equation (18) we get

$$\left|\frac{C_1}{A_1}\right|^2 = \left|\frac{2k_1}{k_1 + ik_3}\right|^2$$

$$\text{or } \left|\frac{C_1}{A_1}\right|^2 = \frac{4k_1^2}{k_1^2 + k_3^2}$$

$\therefore$ The probability at $x = 0$ is given by

$$|C_1|^2 = \left(\frac{4k_1^2}{k_1^2 + k_3^2}\right)|A_1|^2$$

$$\text{or } |C_1|^2 = \left[\frac{4\left(\frac{2mE}{\hbar^2}\right)}{\frac{2mE}{\hbar^2} + \frac{2m(V_o - E)}{\hbar^2}}\right]|A_1|^2$$

$$\text{or } |C_1|^2 = \frac{4E|A_1|^2}{E + (V_o - E)}$$

$$\text{or } |C_1|^2 = \frac{4E}{V_o}|A_1|^2 \quad \ldots\ldots (21)$$

$\Rightarrow$ The probability is finite since $E < V_o$. Hence the probability of finding the particle in the forbidden region of positive x can be done by integrating the wavefunction over the x values from 0 to ∞, which will be finite and directly proportional to $|C_1|^2$. This is an example of nanophysical tunnelling effect, a particle can be sometimes found where its energy is negative is $E < V_0$ and therefore classically forbidden. Actually the wave penetrating a small distance from the boundary into the Region II is continuously reflected till all the incident light is turned back into Region I. Due to such continous reflection the amplitude of the wave penctrating into Region II falls off exponentially. Classically a particle of energy $E < V_o$ can never penetrate into Region II because its kinetic energy would be negative. On the other hand in the nanophysical world there is finite probability of the particle wave penetrating a short distance into the classically forbidden Region II and decaying exponentially.

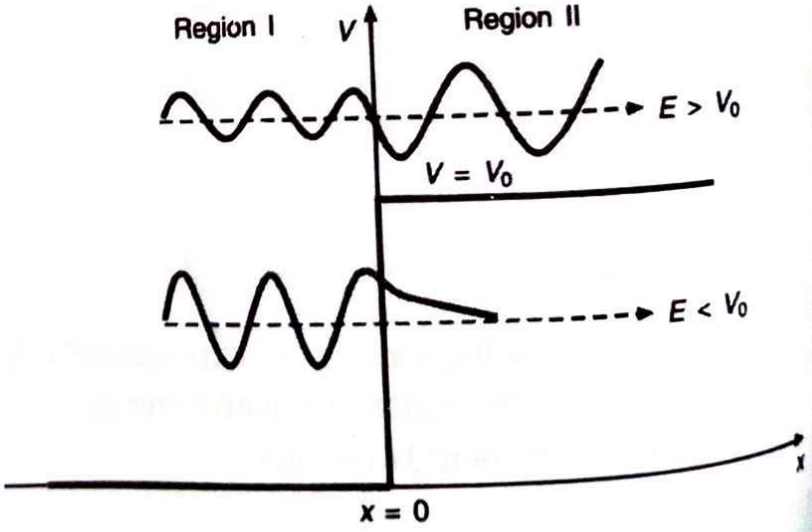


Fig2.1.2(b) Wavefunctions for a step potential.

In the case of $E > V_o$ as per equation (7), $|C_1| > |A|$ since $k_1 > k_2$. Hence the amplitude of the transmitted

wave is more than the amplitude of incident wave. Since the kinetic energy of the particle is more in Region I, hence the de Broglie wavelength is less in Region I with respect to Region II as shown in Fig 2.1.2(b). On the other hand in the case of $E < V_0$ the transmitted wave decays exponentially within a very short distance of Region II as shown in Fig 2.1.2(b).

Now the incident particle wave and the reflected particle in the Region I ($x < 0$) superpose to form standing wave which is given by

$$\psi_1(x) = 2|A_1|\cos(k_1 x + \epsilon) \qquad \ldots\ldots (22)$$

This obtained from equation (14) with $|B_1| = |A_1|$ and ϵ is the phase shift of the standing wave. The standing wave will form ripples whenever a particle wave is reflected from a barrier with a wavelength of $\lambda = \frac{2\pi}{k_1}$ and $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$. These repples are shown in Fig 2.1.2(c).

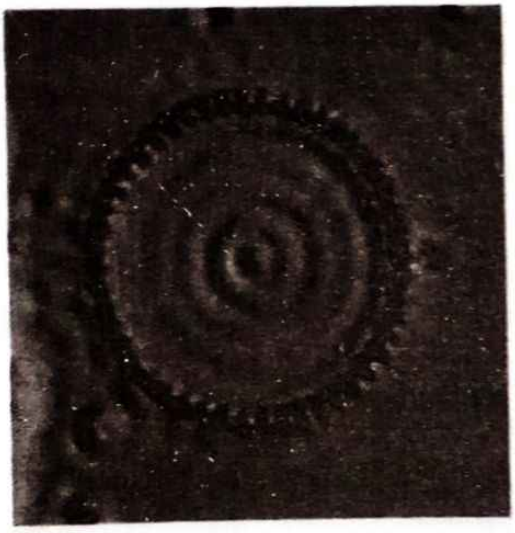


Fig. 2.1.2(c) Scattered electrons formed standing wave 'ripples' inside a ring of Fe atoms on a Cu surface.

2.1.3 Potential box (Nanodot)

Consider a particle restricted to move in a 3D box of volume L^3 with impenetrable walls as shown in Fig 2.1.3(a).

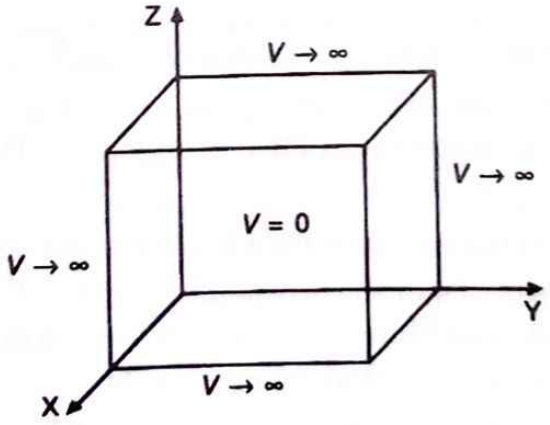


Fig. 2.1.3(a) Three-dimensional infinite potential well.

The schrodinger equation in 3D for a free particle restricted to move in a box is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad \text{.....(1)}$$

where $\vec{r}$ is the position vector and

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The solutions to equation (1) are given by

$$\psi_n(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L} \quad \text{....(2)}$$

$$\text{and } E_n = \left[\frac{h^2}{8mL^2}\right]\left(n_x^2 + n_y^2 + n_z^2\right) \quad \text{....(3)}$$

where $n_x = 1,2,3.....$ $n_y = 1,2,3.....$ and $n_z = 1,2,3.....$

If the box is of unequal dimensions L_x, L_y and L_z then equation (3) can be rewritten as

$$E_{n_x n_y n_z} = \left[\frac{h^2}{8m}\right]\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \quad \text{....(4)}$$

It is clear from equation (4) that the energy is dependent on three quatum numbers n_x,n_y and n_z.

The lowest energy for $n_x=1$, $n_y=1$ and $n_z=1$ is given by

$$E_{111} = \frac{h^2}{8m}\left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right) \quad \text{....(5)}$$

The next energy level corresponds to E_{211} which is same as E_{121} and E_{112}. Hence the second energy level has three states for same energy as ψ_{211},ψ_{121} and ψ_{112}. The number of states that have the same energy is called the degeneracy of that energy level. Therefore the second energy level is three fold degenerate.

Nanoparticles with a fraction of a nanometer to a few tens of nanometre size can be considered as the examples of 3D confinement of carriers in a small 3D space. Fig-2.1.3(b) shows the field emission scanning electron microscopy (FESEM) image of a Si nanoparticle which is marked by an arrow. The diameter of the particle is around 15nm. Fig-2.1.3(c) shows the high resolution transmission eletron microscopy (HRTEM) image of a similar kind of Si nanoparticle of diameter around 15 nm.

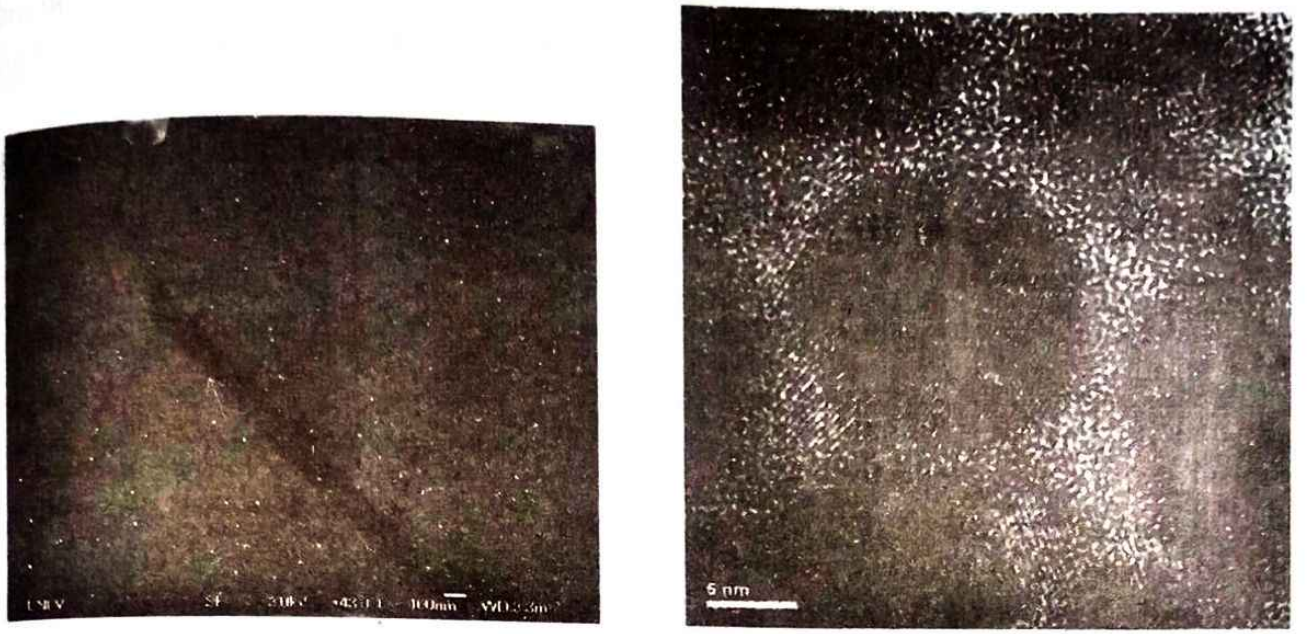


Fig. 2.1.3(b) FESEM image of a single Si nanoparticle shown by the arrow, and **(b)** HRTEM image of a 15 nm Si nanoparticle. Oriented atomic planes are visible inside the nanoparticle [13].

2.1.4-Electron trapped in 2D Plane (Nanosheet):

Consider an electron is trapped in a 2D plane. The electron is confined along one dimension ie along Z-axis to a very small thickness t and it is free to move along x-axis and y-axis as shown in Fig-2.1.4(a).

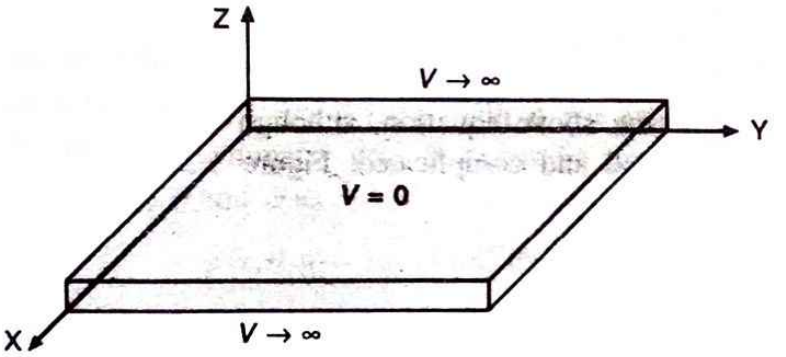


Fig. 2.1.4(a) Two-dimensional space. Particles can move along X- and Y-directions freely but confined along Z-direction by a small distance *t*.

In nanophysics this is the case of nanosheet where carriers are allowed to move along a two dimensional plane.

In this cas the equations for wave function and energy are given by

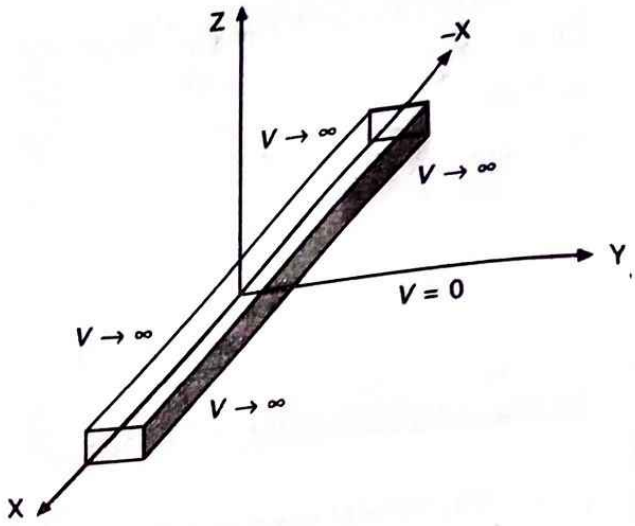
$$\Psi_n(x,y,z) = \left(\frac{2}{t}\right)^{\frac{1}{2}} \sin\frac{n_z \pi z}{t} e^{ik_x x} e^{ik_y y} \qquad \ldots.(1)$$

$$\text{and } E_n = \left(\frac{h^2}{8mt^2}\right) n_z^2 + \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} \qquad \ldots.(2)$$

Where the quantum number n_z is called the sub-band index and for n = 1 the carrier is assumed to be in the first sub-band. In general the election motion in a semiconductor band is described by introducing the effective mass of electrons and holes.

2.1.5.-Electron moving in ID (Nanowire/ Nanorod/Nanobelt)

Consider an electron moving in ID as shown in Fig.2.1.5(a).



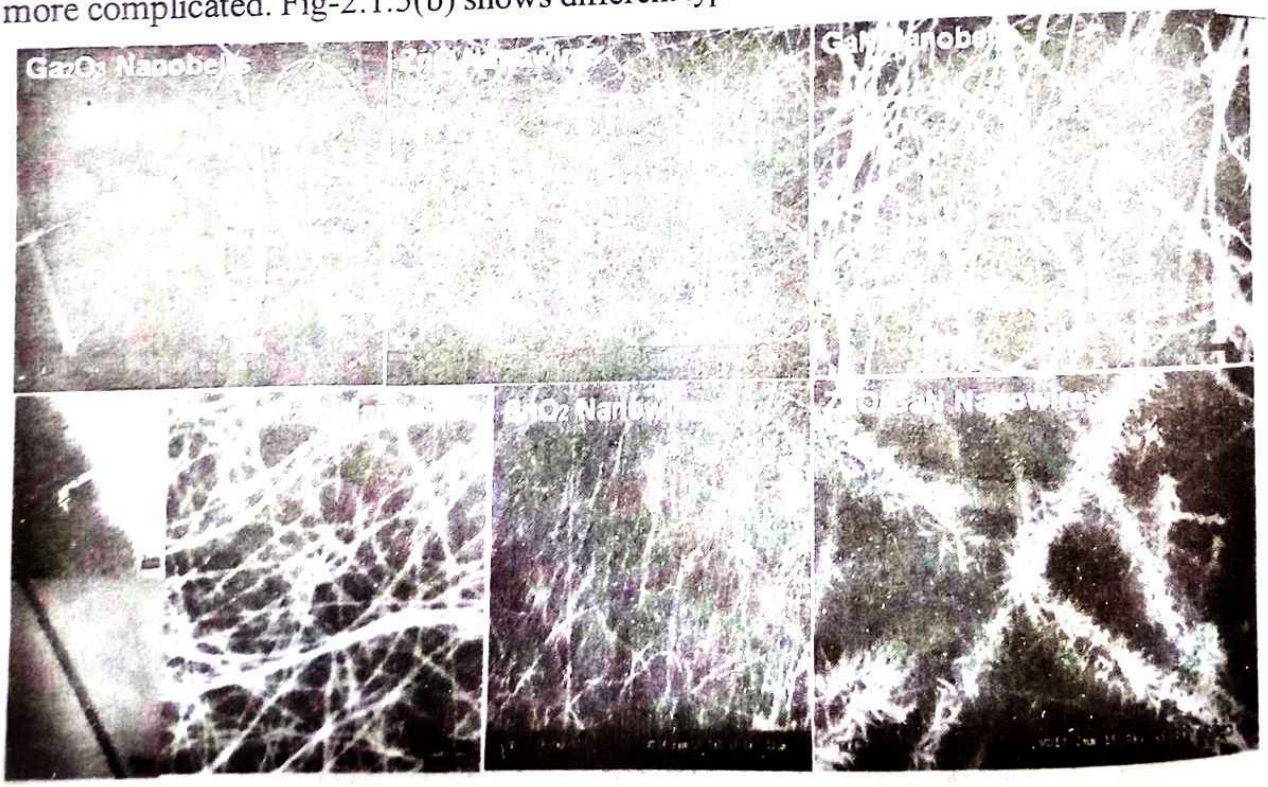
In nanophysics this is the case of nano wire or nanorod or nanobelt where the carriers are confined in two dimensions (Y and Z) to small dimension t (assuming square cross section t^2) and allowed to move freely along X-axis.

In this case the equations for wavefunction and energy are given by

$$\psi_n(x,y,z) = \left(\frac{2}{t}\right)\sin\frac{n_y\pi y}{t}\sin\frac{n_z\pi z}{t}e^{ik_x z} \quad \ldots(1)$$

$$\text{and } E_n = \left(\frac{h^2}{8mt^2}\right)\left(n_y^2 + n_z^2\right) + \frac{\hbar^2 k_x^2}{2m} \quad \ldots(2)$$

In nanophysics the motion of carriers in carbon nanotubes or similar kind of nanowires can be treated by the above equations qualitatively but the actual bound states and energy equations are more complicated. Fig-2.1.5(b) shows different types of ID nanostructures.



2.2 QUNTUM CONFINEMENT OF CARRIERS IN NANOSTRUCTURES AND ITS CONSEQUENCES

In nanostructure materials the energy level scheme depends on the size, shape and nature of the materials. Proper formation of the potential energy terms along with the Schrodinger equation and wave functions show that the bandgap of the nanocrystalline material increases with respect to the bulk value *i.e.* there will be a blue-shift (ΔE) of the bandgap as the crystal size approaches from bulk size to lower dimensions of nanometric range as shown below.

$$\Delta E = E_{g(nano)} - E_{g(bulk)} = \frac{n^2h^2}{8\mu^* r^2} - \frac{1.8e^2}{\epsilon r} - 0.248E_R^*$$

where r = radius of the nanoparticle

n = integer

$\mu^* = \left[\left(m_h^*\right)^{-1} + \left(m_e^*\right)^{-1}\right]^{-1}$ = reduced mass of the effective masses of the electron and hole respectively .

ϵ = dielectric constant of the semiconducting material.

$E_{R_e}^*$ = Effective Rydberg constant charge of electron or hole.

The first term on the right hand side of equation (1) represents the particle in a box quantum localization energy and has a $\frac{1}{r^2}$ dependence for both electron and hole. The second term represents the coulomb energy with $\frac{1}{r}$ dependence and the third term is responsible for the spatial correlation. The n values larger than I crrespond to the exciton transitions to higher excited states. In the limit of large are the value of $E_{g(nano)}$ approaches that of $E_{g(bluk)}$. The bandgap enhancement in nanostrcture materials is experimentally observed in many semiconducting materials as shown in Fig 2.2(a) and described in Table-2.2. :

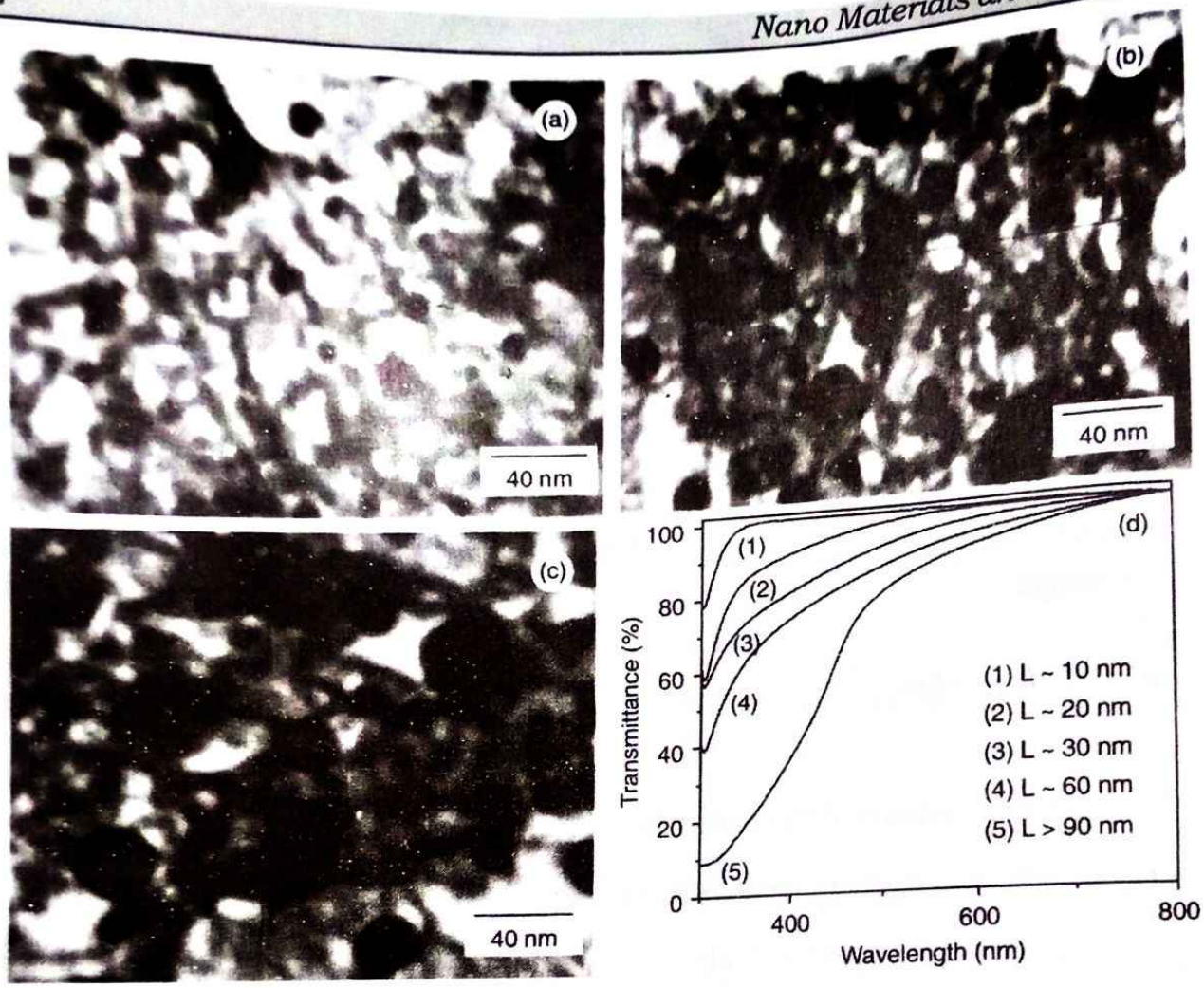


Fig. 2.2(a) TEM images of p-$CuAlO_2$ nanoparticles of average size (L) of **(a)** 10 nm, **(b)** 20 nm and **(c)** 30 nm, and **(d)** optical transmittance spectra of the nanoparticles showing the blue-shift of the band-gap edges with decrease in the particle size, indicating the size-effects of band-gap enhancement in semiconductor nanocrystals.

Increase in the optical band-gap of p-$CuAlO_2$ nanoparticles with decrease in the average particle size, showing the quantum confinement effect of the band-gap enhancement in semiconductor nanocrystals.

Particle size (nm)	Band gap (eV)
> 90 (bulk)	3.34
60	3.60
30	3.72
20	3.84
10	3.94

The optical and luminescent properties of nanoparticles are generally dependent on this quantum size effect. The CdSe quantum dots are found to emit different colours as their size changes as shown in Fig 2.2(b).

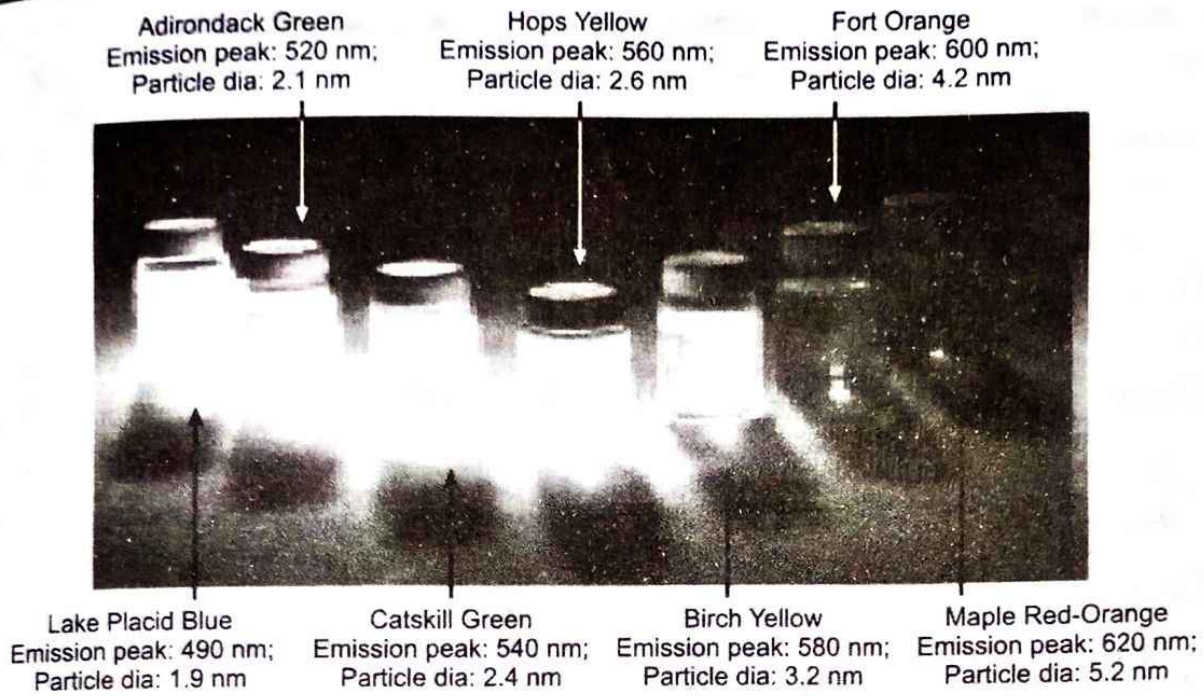


Fig.2.2(c) Images of core-shell CdSe/ZnS quantum dots stored in vials, showing emission of different colours with change in the size of the QDs. Data collected from evident technologies [6].

As the size decreases the emitted light wavelength moves towards blue region. Hence by changing the size of the quantum dots one can produce different wavelengths of light through them under radiation. Similarly Fig-2.2(c) shows the size effect in the photo-luminescence spectra of P-$CuAlO_2$ nanoparticles. As the size decreses the emission peak shifts towards low wavelength (blue-shift) region.

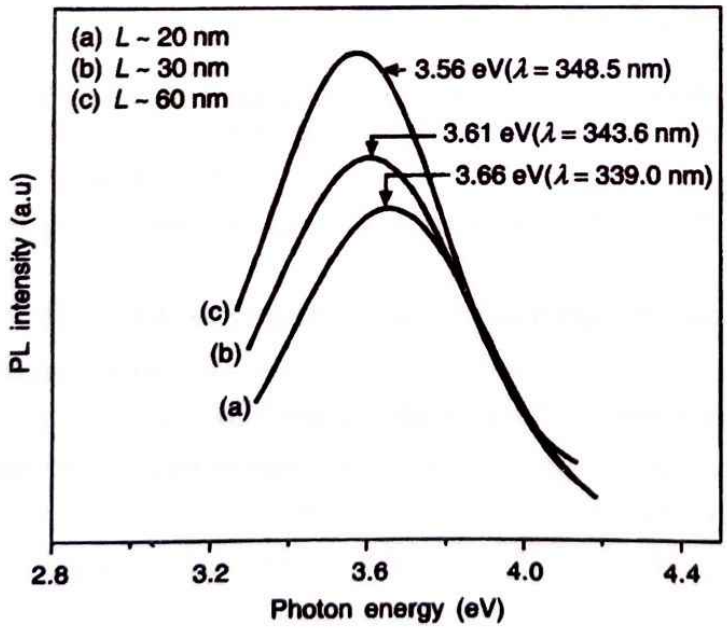


Fig. 2.2(c) Photoluminescence spectra of p-$CuAlO_2$ nanoparticles showing a blue-shift in the emission peak with a decrease in the particle size [17].

SUMMARY

- Quantum confinement is the change of electronic and optical properties when the material is of sufficiently small size i.e 10 nanometres or less.
- The bandgap increases with the decrease in the size of the nanosructure.
- The bandgap and wavelength are inversely related to each other.
- The wavelength decreases with the decrease in size of the nanostructure.
- The time-dependent Schrodinge equation in 1D is given by

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_{(x,t)} + U_{(x,t)}\psi_{(x,t)} = i\hbar\frac{\partial}{\partial t}\psi_{(x,t)}$$

- The time – dependent Schrodinger equation in 3D is given by

$$[-\frac{\hbar^2}{2m}\nabla^2 + U_{\vec{(r,t)}} - i\hbar\frac{\partial}{\partial t}]\psi_{\vec{(r,t)}} = 0$$

- The time - independent Schrodinger equation in 1 D is given by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{(x)} + U_{(x)}\psi_{(x)} = E\psi_{(x)}$$

- The time-independent schrodinger equation in 3D is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{(r)}} + U_{\vec{(r)}}\psi_{\vec{(r)}} = E\psi_{\vec{(r)}}$$

- The normalized wavefunction $\psi_n(x)$ is known as eigenfunction and is given by

$$\psi_n(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\frac{n\pi x}{L}$$

- According to the uncertainty principle the lowest energy of the electron cannot be zero.
- The transmission coefficient is defined as the probability ratio of transmitted particle wave with respect to the probability ratio of incident particle wave.
- The reflection coefficient is defined as the probability ratio of reflected particle wave with respecto to protability ratio of incident particle wave.
- The schrodinger equation in 3D for a free particle restricted to move in a box is given by $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$
- The number of states that have the same energy is called the degeneracy of that energ level.

- Nanoparticles with a fraction of a nanometer to a few tens of nanometre size can be considered as the examples of 3D confinement of carriers in a small 3D space.
- In nanophysics this is the case of nanosheet where carriers are allowed to move along a two dimensional plane.
- In nanophysics this is the case of nano wire or nanorod or nanobelt where the carriers are confined in two dimensions (Y and Z) to small dimension t (assuming square cross section t^2) and allowed to move freely along X-axis.
- In nanostructure materials the energy level scheme depends on the size, shape and nature of the materials.
- The bandgap enhancement in nanostrcture materials is experimentally observed in many semiconducting materials.
- The optical and luminescent properties of nanoparticles are generally dependent on this quantum size effect.
- As the size decreases the emitted light wavelength moves towards blue region. Hence by changing the size of the quantum dots one can produce different wavelengths of light through them under radiation.

QUESTIONS

Long Answer Type Questions :

1. Write one dimensional time independent Schrodinger equation and apply this equation to explain the quantum confinement of a particle trapped in an infinite potential well.
2. Discuss the application of Schrodinger equation to a particle moving along the positive x-axis toward a potential step.
3. Apply Schrodinger wave equation to explain the quantum confirement of a particle in 3D trapped inside a potential box.
4. Explain the quantum confinement of an electron in one dimension and it is free to move along two other axes.
5. Explain the quantum confinement of an electron cnfined in two dimensions and it is free to move m another directional axis.
6. Explain quantum confinement effect in nano-structured materials and its consequences.

Very Short Answer Type Questions :

1. What is quantum confinement ?
2. Write the time dependent schrodinger equation in 1D.
3. Write the time independent schrodinger equation in 1D.
4. Write the time independent schrodinger equation in 3D.
5. Write an expression for the normalization constant for the infinite potential well.
6. What is eigen function ?
7. Write an expression for the eigen function for infinite potential well.
8. Write an expression for the eigen energy for infinite potential well

9. Write an expression for transmission coefficient for a potential step when $E > V_0$.
10. Define reflection coefficient for a potential step and write an expression for it when $E > V_0$.
11. Write an equation for the wave function of a potential box.
12. Write an expression for the energy of particle in a potential box.
13. Write an equation for the wave function of an electron trapped in 2D plane nano sheet.
14. Write an equation for the energy of an electron trapped 2D plane radio sheet.
15. Write an expression for the wave function of an electron moving in1D nanowire.
16. Write an expression for the energy of an electron moving in 1D nanowire.
17. What is blue shift ?
18. Which properties of nano-particles are dependent on quantum size effect ?

❑